Pearson Edexcel IAS CHEMISTRY

WCH11/WCH12

REVISION GUIDE

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Unit 1: Structure, Bonding and Introduction to Organic Chemistry

Unit 2: Energetics, Group Chemistry, Halogenoalkanes and Alcohols

Unit 1: Structure, Bonding and Introduction to Organic Chemistry

Topic 1: Formulae, Equations and Amount of Substance

a demonstrate an understanding of the terms atom, element, ion, molecule, compound, empirical and molecular formulae

- An **element** is a substance that cannot be broken down by chemical means into other substances.
- All the atoms in an element have the same atomic number which is the number of protons in an atom.
- An **atom** is the smallest part of an element that can take part in a chemical change. Atoms have no charge, they are neutral.
- The **mass number** of an atom is the sum of protons and neutrons in that atom.
- A **compound** is formed when two or more elements are chemically bonded together.
- A **molecule** is the smallest part of the covalent compound or element that can exist on its own.
- Ionic compounds are formed from ions.
- An ion is formed when an atom gains or loses one or more electrons – ions are therefore, charged particles.

b write balanced equations (full and ionic) for simple reactions, including the use of state symbols

A balanced chemical equation tells us not only what is reacting and what is produced but also in what proportions the atoms combine. A balanced chemical equation has the same number of atoms on each side.

Example

Unbalanced Equation: $H_2 + O_2 \rightarrow H_2O$
Balanced equation: $2H_2 + O_2 \rightarrow 2H_2O$

c demonstrate an understanding of the terms relative atomic mass, amount of substance, molar mass and parts per million (ppm), e.g. gases in the atmosphere, exhausts, water pollution

- The **relative atomic mass** of an element is the average (weighted) mass of the element's isotopes relative to one – twelfth of the mass of a carbon – 12 atom.
- The **mole** is the unit of chemical amount or **amount of substance.**
- 1 mole is the amount of substance that contains as many particles as there are atoms in exactly 12g of carbon – 12.
- The mass, in grams of 1 mole of substance is known as **molar mass**, Mr.
- $amount = \frac{mass}{Mr}$
- $amount = volume\ x\ concentration$
- Small concentration can be expressed in parts per million, ppm.

$$ppm = \frac{mass\ of\ component}{mass\ of\ solution} \times 10^6$$

Example: There is 2g of organophosphate pollution in 1.5 million grams of solution.

- $ppm = \frac{2}{1500000} \times 10^6$
- $ppm = 1.3$

d calculate the amount of substance in a solution of known concentration (excluding titration calculations at this stage), e.g. use data from the concentrations of the various species in blood samples to perform calculations in mol dm −3

Example

Solute	Normal blood level
Creatinine (a waste product of muscle metabolism)	60 -120 mmol dm^{-3}
Urea (a waste product of protein metabolism)	3.5 – 6.5 mmol dm^{-3}
Na^+ (sodium ions)	135 – 145 mmol dm^{-3}
K^+ (potassium ions)	3.5 - 5.0 mmol dm^{-3}

An average person has 5dm^3 of blood. Using the table above, find the minimum mass of sodium ions in the blood of an average person.

mole = volume x concentration
= 5 x 135/1000
= 675/1000

mass = mole x Mr
= 675/1000 x 23
= 15.5 g

e use chemical equations to calculate reacting masses and vice versa using the concepts of amount of substance and molar mass

- The **molar volume** of a gas is the volume of 1 mole of it.
- For all gases, this is 24 dm^3 mol^{-1} at **standard temperature** (25°C or 298K) and **pressure** (1 atm)

Example

When 11.2 g of iron reacted with excess chlorine, 32.0 g of iron (III) chloride were formed. What is the equation for the reaction?

amount of iron = $\frac{11.2\text{g}}{56\text{ g }mol^{-1}} = 0.200\ mol$

amount of iron (III) chloride = $\frac{32.0}{162.5} = 0.197\ mol$ = 0.200 mol (1 s.f)

Therefore, the equation must be:

$$2Fe + 3Cl_2 \rightarrow 2FeCl_3$$

f use chemical equations to calculate volumes of gases and vice versa using the concepts of amount of substance and molar volume of gases, e.g. calculation of the mass or volume of CO2 produced by combustion of a hydrocarbon (given a molar volume for the gas)

Example

What volume of oxygen at standard temperature and pressure is needed to burn exactly 6 dm^3 methane according to the following equation?

$$\mathbf{CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)}$$

Mole of methane = volume x concentration
= 6 x 24
= 144

Mole of oxygen = 2 x 144
= 288

Volume of oxygen = 288/24
= 12 dm^3

g use chemical equations and experimental results to deduce percentage yields and atom economies in laboratory and industrial processes and understand why they are important

Percentage yield

No atoms are gained or lost in a chemical reaction. However, it is unusual to obtain the theoretical maximum amount of a product:

- the reaction may be reversible
- some of the reactants or products may be left behind in the apparatus, such as when filtering or pouring
- some of the reactants may react in ways different to the expected reaction (**side reaction**, which produce **by-products**).

The amount of a product obtained is the yield. When compared with the maximum theoretical amount as a percentage, it is called **percentage yield**:

- $Percentage\ yield = \frac{actual\ \ mass}{theoritical\ mass} \times 100\%$

Example

Magnesium reacts with oxygen according to the equation:

$2Mg(s) + O_2(g) \rightarrow 2MgO\ (s)$

When a student heated a 2.00 g coil of magnesium ribbon in a crucible, she produced 3.00 g of the oxide. What is the theoretical yield? And what percentage yield was achieved?

amount of Mg = 2/24 = 0.083 mol
amount of MgO = 0.083 mol

theoretical mass of MgO = 40 x 0.083
= 3.32 g

Percentage yield = $\frac{3}{3.32}$ x 100%
= 90.4%

Atom economy

- Atom economy is a measure of the amount of starting materials that end up as useful products.
- $Atom\ economy = \frac{mass\ of\ atoms\ in\ required\ product}{total\ mass\ of\ atoms\ in\ reactants} \times 100\%$
- A reaction with a high economy makes use of most of the atoms of the reactants, with few wasted as by-products.
- This reduces the amount of waste products a company has to deal with, which in turn reduces the cost of waste treatment.
- Atom economy can be improved by finding uses for any by-products

Example

Calculate the atom economy of using copper oxide and sulfuric acid to make copper sulfate in the solution:

$CuO\ (s) + H_2SO_4\ (aq) \rightarrow CuSO_4\ (aq) + H_2O\ (l)$

Atom economy = $\frac{mass\ of\ copper\ sulfate}{masses\ of\ copper\ oxide + sulfuric\ acid}$ x 100%
= $\frac{63.5+32.0+(4\times16.0)}{(63.5+16.0)+(2+32.0)+(4x16)}$ x 100%
= 89.9%

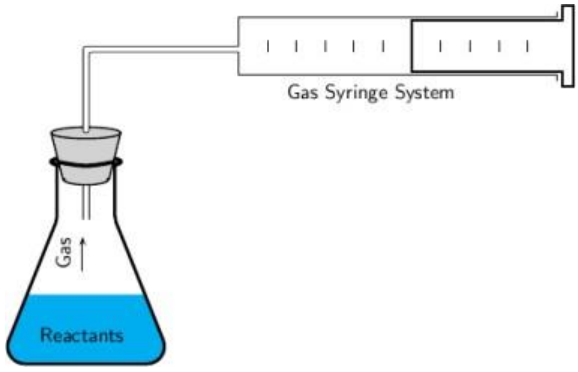
h demonstrate an understanding of, and be able to perform, calculations using the Avogadro constant

- The number of atoms in exactly 12g of carbon – 12 is 6.02 x 10^{23}. This is known as the Avogadro constant and has the unit particles per mole.
- $Number\ of\ particles = mole\ \times Avogadro\ constant$

i analyse and evaluate the results obtained from finding a formula or confirming an equation by experiment, e.g. the reaction of lithium with water and deducing the equation from the amounts in moles of lithium and hydrogen

Example

A reaction between lithium and water at 25°C has been carried out in the lab and quantities of some of the reacting materials have been measured.



They reacted 0.035 g of lithium with water and 60 cm^3 of hydrogen was collected in a gas syringe. Use this information to confirm the correct equation:

a) **$Li (s) + 2H_2O (l) \rightarrow Li(OH)_2(aq) + H_2 (g)$**
b) **$2Li (s) + 2H_2O (l) \rightarrow 2LiOH (aq) + H_2 (g)$**

Amount of Li = 0.035/6.9 = 0.005 mol
Amount of H_2 = 60/24000 = 0.0025 mol

0.005/0.0025 = 2. Therefore, when 2 mol of lithium reacts with water, 1 mol of hydrogen gas is formed. So, **(b) is correct**.

j make a salt and calculate the percentage yield of product, e.g. preparation of a double salt (ammonium iron(II) sulfate from iron, ammonia and sulfuric acid)

Salts are ionic compounds. The positive ion, or cation, is usually a metal ion or an ammonium ion, NH_4^+. The negative ion comes from an acid such as SO_4^- in H_2SO_4.

A **double salt** contains more than one cation or anion. They form when a solution of two simple salts crystallises to form a single substance.

- Salts can be produced by neutralizing acids with an alkali, carbonate or metal oxide or hydroxide.
- Salts can be produced by reacting acids with reactive metals.

- A soluble salt must be crystallised from a saturated solution – concentrate the solution by driving off some of the water, leaving it to evaporate and then filtering.
- An insoluble salt forms a precipitate and can be filtered off, washed and dried.

Example

A student prepared a sample of copper (II) nitrate crystals by neutralizing excess dilute nitric acid with 12.35 g copper (II) carbonate, then filtering and evaporating the solution. The crystals were dehydrated and had a mass of 18.05 g. Calculate the percentage yield.

$CuCO_3 + 2HNO_3 \rightarrow Cu(NO_3)_2 + H_2CO_3$

Amount of $CuCO_3$ = 12.35/(63.5 + 12 + 16x3)
= 0.1 mol

Amount of $Cu(NO_3)_2$ = 0.1 mol

Mass of $Cu(NO_3)_2$ = 0.1 x [63.5 + 2{14 + (16 x 3)}]
= 18.75 g (theoritical)

Percentage yield = 18.05/18.75 x 100%
= 96.3%

k carry out and interpret the results of simple test tube reactions, such as displacements, reactions of acids, precipitations, to relate the observations to the state symbols used in equations and to practise writing full and ionic equations.

(s) → solid
(l) → liquid
(g) → gas
(aq) → aqueous

Topic: Energetics

a demonstrate an understanding of the term enthalpy change, ΔH

When a reaction occurs at constant pressure and gives or takes in energy there is an enthalpy change, ΔH, between the system (reactants and products) and its surroundings.

$$\Delta H = H_{products} - H_{reactants}$$

b construct simple enthalpy level diagrams showing the enthalpy change

Exothermic reaction

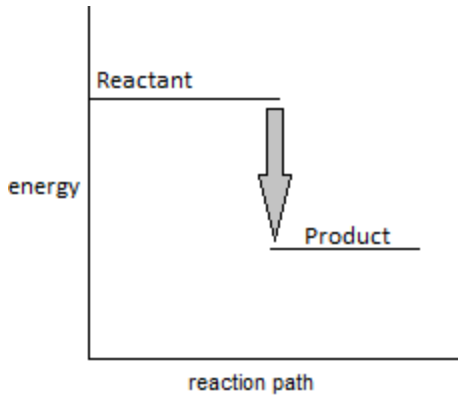


Fig: Energy Level Diagram

Endothermic reaction

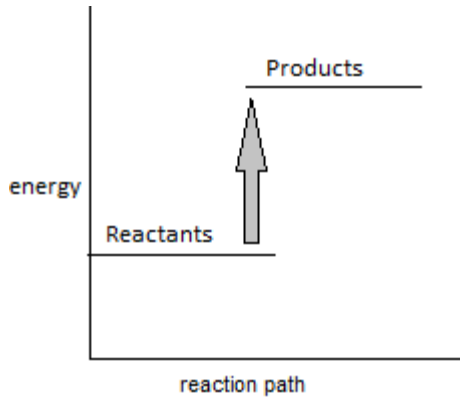


Fig: Energy Level Diagram

c recall the sign of ΔH for exothermic and endothermic reactions, e.g. illustrated by the use of exo - and endothermic reactions in hot and cold packs

An exothermic reaction has a negative ΔH: $\Delta H < 0$. This is because the products are at lower energy level than the reactants – the products have less energy than the reactants. Energy has been given out by the system to the surroundings – the surroundings get hotter.

An endothermic reaction has a positive ΔH: $\Delta H > 0$. This is because the products are at higher energy level than the reactants – the products have more energy than the reactants. Energy has been absorbed by the system from the surroundings – the surroundings get colder.

d recall the definition of standard enthalpy changes of reaction, formation, combustion, neutralisation and atomisation and use experimental data to calculate energy transferred in a reaction and hence the enthalpy change of the reaction. This will be limited to experiments where substances are mixed in an insulated container and combustion experiments

Standard Conditions

Enthalpy changes depend on the temperature and pressure at which the reactions occur. Therefore, a set of standard conditions is necessary to make measurements comparable. Standard conditions are:

- 1 atm pressure at 298 K (25°C)
- Reacting substances are in their normal physical states at 1 atm and 298 K
- Solutions have a concentrations of 1 mol/dm^3

An enthalpy change measured under these conditions is called **standard enthalpy change** and has the symbol **$\Delta H^{\ominus}$**.

$\Delta H^{\ominus}$ is expressed per mole of substance reacting, and the units are kJ/mol.

Definitions and symbols

- The **standard enthalpy change of reaction, $\Delta H^{\ominus}$**, is the enthalpy change when the number of moles of reactants react under standard conditions as specified in the reaction.
- The **standard enthalpy change of formation of a compound, $\Delta H_f^{\ominus}$**, is the enthalpy change when 1 mole of the compound is formed from its elements under standard conditions. The standard enthalpy change of formation of any element, in its standard state, is therefore zero. For example, $\Delta H_f^{\ominus}$ [Cl_2 (g)] = 0.
- The **standard change of combustion, $\Delta H_c^{\ominus}$**, is the enthalpy change when 1 mole of the substance is completely burnt in oxygen under standard conditions.
- The **standard enthalpy change of atomization, $\Delta H_{at}^{\ominus}$**, is the enthalpy change when 1 mole of atoms in the gaseous state is formed from the element under standard conditions. For example, $\Delta H_f^{\ominus}$ [$\frac{1}{2}Cl_2$ (g) → Cl (g)] is not zero, because energy must be transferred to break bonds in the Cl_2 molecules.
- The **standard enthalpy change of neutralization** is the enthalpy change when 1 mole of water is formed by the reaction of an acid with an alkali under standard conditions.

e recall Hess's Law and apply it to calculating enthalpy changes of reaction from data provided, selected from a table of data or obtained from experiments and understand why standard data is necessary to carry out calculations of this type

Hess's law states that

- The total enthalpy change for a reaction is independent of the route taken, provided the initial and final conditions are same.

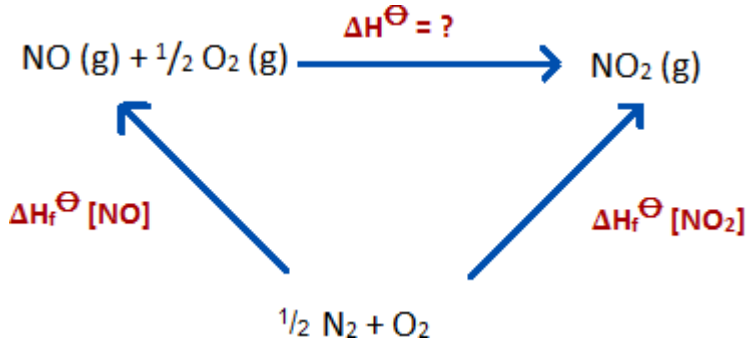
In other words, for any chemical change, the enthalpy change is the same whatever reaction route is taken.

Hess's law is used to calculate the standard enthalpy change for reactions that are difficult to measure or that cannot be measured directly. The requirements are that:

- There are two routes between the reactants and products to be able to draw a Hess cycle
- The data for enthalpy changes for one route is given.

If the standard enthalpy changes of formation of nitrogen (II) oxide, NO and nitrogen (IV) oxide, NO_2 are + 90.2 kJ mol^{-1} and + 33.2 kJ mol^{-1} respectively, calculate $\Delta H^{\ominus}$ for the change:

$NO\ (g) + ½\ O_2\ (g) \rightarrow NO_2\ (g)$



$90.2 + \Delta H^{\ominus} = 33.2$

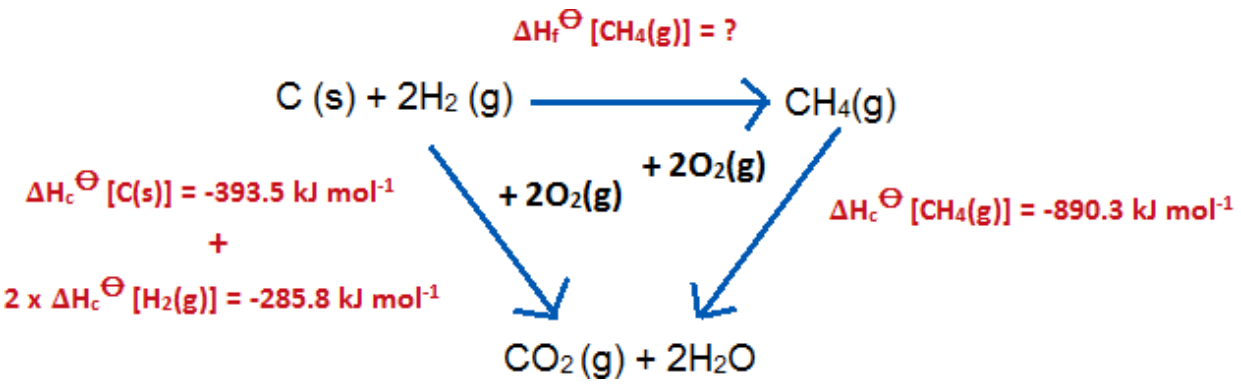
$\Delta H^{\ominus} = -57.0$ kJ mol^{-1}

The direct route for the formation of methane is:

$C(s) + 2H_2(g) \rightarrow CH_4\ (g)$

The standard enthalpy changes of combustion, $\Delta H_c^{\ominus}$ of carbon, hydrogen and methane are -393.5 kJ mol^{-1}, -285.8 kJ mol^{-1}, and -890.3 kJ mol^{-1} respectively.

Note that under standard conditions the normal state of water is liquid – the gas condenses.


$\Delta H_f^\ominus [CH_4(g)] = ?$
C (s) + 2H2 (g)
CH4(g)
+ 2O2(g)
+ 2O2(g)
$\Delta H_c^\ominus [C(s)] = -393.5$ kJ mol-1
+
2 x $\Delta H_c^\ominus [H_2(g)] = -285.8$ kJ mol-1
$\Delta H_c^\ominus [CH_4(g)] = -890.3$ kJ mol-1
CO2 (g) + 2H2O

$\Delta H_f^\ominus[CH_4(g)] + (890.3) = -393.5 - 2(285.8)$

$\Delta H_f^\ominus[CH_4(g)] + (890.3) = -74.8$ kJ mol^{-1}

f evaluate the results obtained from experiments using the expression: energy transferred in joules = mass × specific heat capacity × temperature change and comment on sources of error and assumptions made in the experiments.

Using an insulated coffee-cup calorimeter a student mixed 50 cm^3 each of 2.0 mol dm^{-3} HCl and 2.0 mol dm^{-3} NaOH. They both started at 23.2°C and the final temperature was 36.5°C. Calculate the enthalpy change of neutralization per mole of acid. Specfic heat capacity = 4.2 J g^{-1} K^{-1}

Temperature rise = 36.5 – 23.2 = 13.3°C

Enthalpy change = mcΔT
= (50 + 50) x 4.2 x 13.3
= 5.6 kJ

Amount of HCl = volume x concentration
= 50/1000 x 2.0
= 0.10 mol

Enthalpy change per mole = 5.6/0.1
= 56.0 kJ mol^{-1}

Since, it is an exothermic reaction, the enthalpy change is – 56.0 kJ mol^{-1}

Assumptions made in the calculation:

- All the energy produced by the burning ethanol is transferred to the water
- No heat is absorbed by the calorimeter
- There is no heat loss to the room or from the surface of the water
- The fuel has combined completely – partial combustion lowers the amount of energy released.

These assumptions give rise to **systematic errors** – inaccuracies in the calculated enthalpy change. **Random errors** also rise from measurement uncertainties – for example in the mass of water or the recorded temperatures.

The following types of experiments should be performed:

i experiments in which substances are mixed in an insulated container and the temperature rise measured

ii simple enthalpy of combustion experiments using, e.g. A series of alcohols in a spirit burner

iii plan and carry out an experiment where the enthalpy change cannot be measured directly, e.g. The enthalpy change for the decomposition of calcium carbonate using the enthalpy changes of reaction of calcium carbonate and calcium oxide with hydrochloric acid

g) demonstrate an understanding of the terms bond enthalpy and mean bond enthalpy, and use bond enthalpies in Hess cycle calculations and recognize their limitations. Understand that bond enthalpy data gives some indication about which bond will break first in a reaction, how easy or difficult it is and therefore how rapidly a reaction will take place at room temperature.

Bond dissociation enthalpy is the energy associated with 1 mole of a particular bond. It is often referred to as bond enthalpy. It is the energy:

- Required to break 1 mole of bonds
- Released on making 1 mole of bonds

For example, for the reaction Cl_2 (g) → 2Cl (g) ΔH = +243.4 kJ/mol. Note that this is positive – energy is needed to break Cl – Cl bonds.

Mean bond enthalpy is the mean bond dissociation enthalpy for a particular bond in a range of compounds – it can be used to calculate the enthalpy change for reactions using Hess's law.

Because they use average values taken from many different compounds, enthalpy changes calculated in this way are usually slightly different from those obtained experimentally. Another source of inaccuracy might come in your calculation as bond enthalpies only apply to substances in gaseous state, where many reactions involve solids, liquids or aqueous solutions.

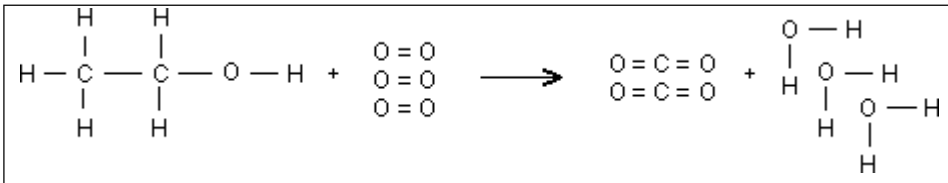
Using mean bond enthalpies

Ethanol is used as fuel. The enthalpy change of combustion can be determined experimentally and also theoretically from mean bond enthalpy data. The reaction is:

$$C_2H_2OH\ (l) + 3O_2 \rightarrow 2CO_2\ (g) + 3H_2O(g)$$

Use these bond enthalpies to calculate the enthalpy change of combustion.

Bond	ΔH/kJ mol^{-1}	Bond	ΔH/kJ mol^{-1}
C – C	347	O – H	464
C – H	413	O = O	498
C – O	358	C = O	805



Bond broken enthalpy = (5 x 413) + 347 + 358 + 464 + (3 x 498)

= 4728 kJ mol^{-1}

Bond making enthalpy = (2 x 2 x 805) + (3 x 2 x 464)

= 6004 kJ mol^{-1}

ΔH = 4728 – 6004

= - 1296 kJ mol^{-1}

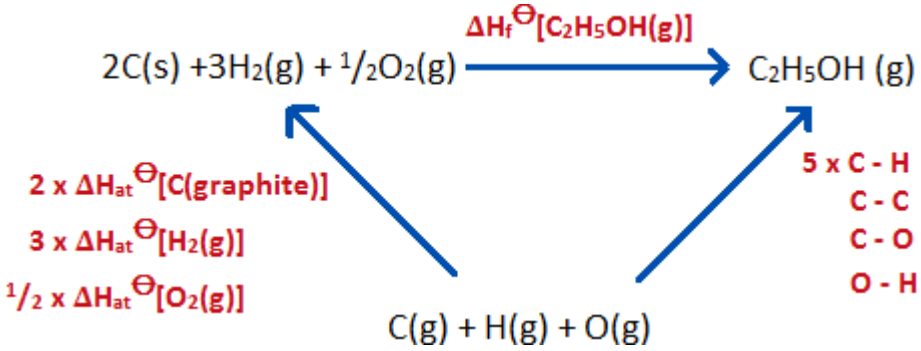
Bond enthalpies in Hess cycle calculations

Using the bond enthalpies from previous example, estimate the enthalpy change of formation of ethanol vapour from its elements. Given the data:

$\Delta H_{at}^{\theta}[C(graphite)] = +718\ kJ\ mol^{-1}$

$\Delta H_{at}^{\theta}[H_2(g)] = +218\ kJ\ mol^{-1}$

$\Delta H_{at}^{\theta}[O_2(g)] = +249\ kJ\ mol^{-1}$



$\Delta H_f^{\theta} + (5 \times 413) + 347 + 358 + 464 = (2 \times 718) + (3 \times 218) + (\frac{1}{2} \times 249)$

$\Delta H_f^{\theta} = 2214.5 - 3234$

$= -1019.5\ kJ\ mol^{-1}$

Bond enthalpy and stability

The larger the bond enthalpy, the stronger the bond. Bond enthalpy data gives an indication of:

- The ease with which a bond will break. The higher the bond enthalpy, the more energy is needed to break the bond, and the less likely it is to break in a reaction.
- Bond will break first in a reaction. Bonds with relatively low bond enthalpies are the easiest and therefore usually the first bonds to break.
- How fast a reaction might be. A reaction that involves breaking bonds with relatively low bond enthalpies is more likely to take place at room temperature than a reaction between molecules held by bonds with high bond enthalpies.

Stability

Compounds having less standard enthalpy of formation are more stable. e.g. hydrogen peroxide ($\Delta H_f^{\ominus} = -187.8$ kJ mol^{-1}) is more **energetically stable** than its elements($\Delta H_f^{\ominus} = 0$).

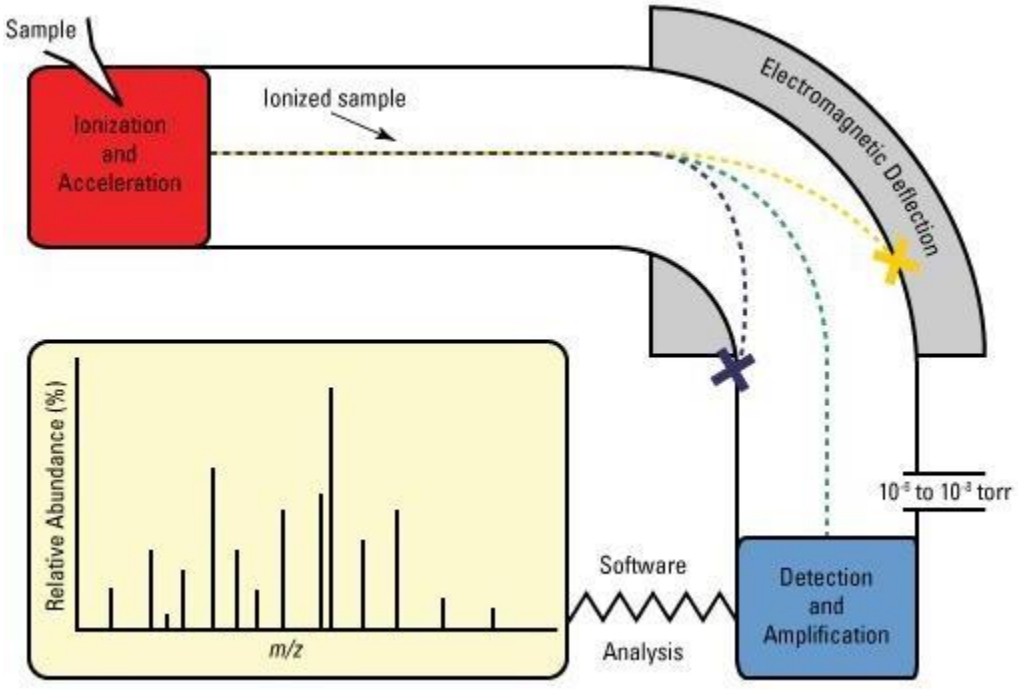
Sometimes, unfamiliar results are found with stability. e.g. nitrogen (II) oxide ($\Delta H_f^{\ominus} = +90.2$) can be stored for long periods at room temperature, as can ethyne ($\Delta H_f^{\ominus} = +228$ kJ mol^{-1}). This is because of the presence of **kinetic stability** (another different kind of stability).

Topic 2: Atomic Structure and the Periodic Table

a recall the definitions of relative atomic mass, relative isotopic mass and relative molecular mass and understand that they are measured relative to 1/12th the mass of a 12C atom

- The **mass number (A)** of an atom is given by the sum of protons (Z) and neutrons in that atom.
- The **atomic number (Z)** is given by the number of protons in an atom.
- **Isotopes** are atoms of the same element (same number of protons) with different number of neutrons, therefore they have different mass numbers.
- **Relative atomic mass** (RAM) is the average (weighted) mass of an element's isotopes relative to 1/12 the mass of ^{12}C atom.
- **Relative isotopic mass** is the mass of an atom of an isotope relative to 1/12 the mass of ^{12}C atom.

b demonstrate an understanding of the basic principles of a mass spectrometer and interpret data from a mass spectrometer to:
i deduce the isotopic composition of a sample of an element, e.g. polonium
ii deduce the relative atomic mass of an element
iii measure the relative molecular mass of a compound

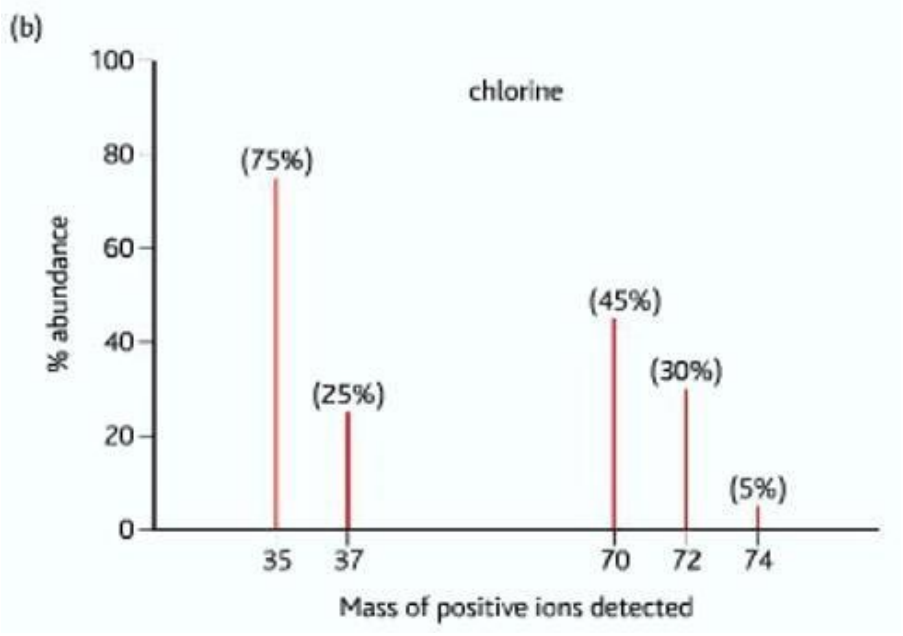


The **mass spectrometer** measures the masses of positive ions formed from atoms:

1. The sample being measured must be in gaseous state for its particles to move through machine. The sample is injected into the mass spectrometer and is first vaporised.
2. The vapour is ionized by bombardment with high-energy electrons and electrons are knocked out of the atoms.
3. The (positive) ions are accelerated by an electric field.
4. They pass through a velocity selector which equalizes their velocity.
5. The ions enter a uniform magnetic field, which deflects them. The amount they are deflected depends on both the mass of the ion and the charge on it. Heavier ions are deflected less than lighter ions, and ions with a small positive charge are deflected less than ions with a bigger positive charge.
6. The field is steadily increased – only ions of a particular $\frac{mass}{charge}$ **ratio** (m/z) pass through at any one time and reach the detector.

   Most of the ions formed have a charge of +1 (loss of electron), so m/z corresponds to the mass of the ion.
7. The detector detects how many ions pass through the machine at each magnetic field setting and each setting of the velocity selector. It shows how many ions of each different mass:charge ratio there are in the sample.

i) A **mass spectrum** shows us the masses of the ions detected and their relative abundance – i.e. the **isotopic composition** of an element.



The mass spectrum of chlorine

ii)

Using the above mass spectrum of chlorine, work out the relative atomic mass of chlorine

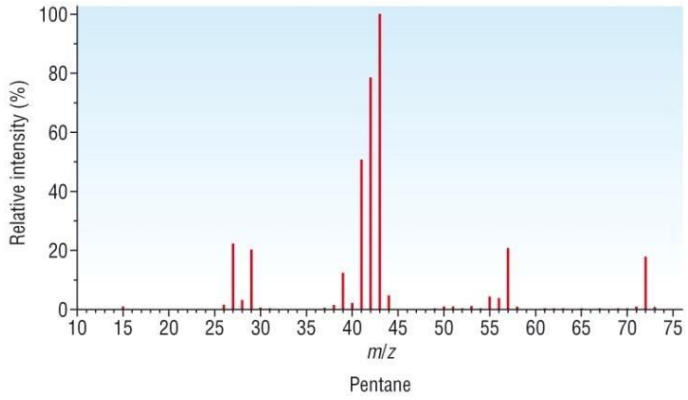
Ar(Cl) = (35 x 75%) + (37 x 25%)
= 35.5

iii)

The mass spectrometer can also be used to measure the relative molecular mass of a compound. Remember, the **relative formula mass** is the sum of the relative atomic masses of all the atoms or ions within the formula. For a covalent molecule this is the **relative molecular mass**.

When the vaporized sample is bombardment with high-energy electrons, not only are electrons knocked off, but the molecule is **fragmented**. The mass spectrum of an organic molecule comprises a number of **peaks** corresponding to the various fragments of differing masses produced during electron bombardment. The peak with the largest m/z value is due to the **molecular ion**, M^+ (also called parent ion). It is formed when a sample molecule loses just one electron and is not fragmented.

The mass spectrum of pentane has a peak at m/z = 72 for the molecular ion $C_5H_{12}^+$. Any compound with the same largest m/z value will have a relative molecular mass of 72.



c describe some uses of mass spectrometers, e.g. in radioactive dating, in space research, in sport to detect use of anabolic steroids, in the pharmaceutical industry to provide an identifier for compounds synthesised for possible identification as drugs

Mass spectrometry has a wide range of applications, some of which are:

- Radioactive dating of archaeological specimens – the percentage abundance of radioactive isotopes is measured
- Space research – identification of molecules detected by planetary probes

- Detection of illegal drugs in athletes' urine samples, such as anabolic steroids – each molecule can be identified by its unique mass spectrum
- Identifying molecules with potential for use as drugs in the pharmaceutical industry – the likely structure of new compounds can be identified from its mass

d recall and understand the definition of ionisation energies of gaseous atoms and that they are endothermic processes

Ionization energy indicates the amount of energy required to remove an electron from an atom. This is an endothermic process since work must be done on an electron in order to overcome the attractive force between it and the nucleus. **It is measured as the energy required to remove 1 mole of electrons from 1 mole of atoms in the gaseous state.**

- The **first ionization energy** (1^{st} I.E) gives us an idea of how easily an atom loses an electron to form a 1+ ion. For example, the first ionization energy of sodium is represented as the equation:
  $Na\ (g) \rightarrow Na^{+}\ (g) + e^{-}$
  1^{st} I.E. = +496 kJ/mol
- The **second ionization energy** (2^{nd} I.E) is the energy required to remove an electron from a 1+ ion to form a 2+ ion. For example:
  $Na^{+}\ (g) \rightarrow Na^{2+}\ (g) + e^{-}$
  2^{nd} I.E. = +4563 kJ/mol

The total energy required to form a 2+ ion from an atom is the sum of the first and second ionization energies.

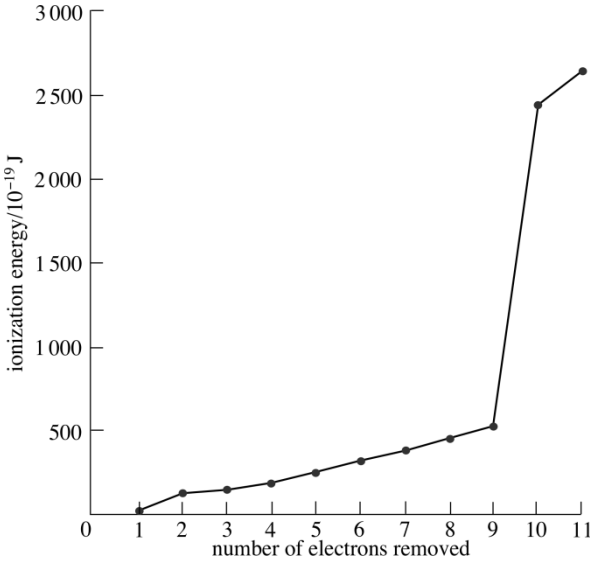
e recall that ideas about electronic structure developed from:
i an understanding that successive ionisation energies provide evidence for the existence of quantum shells and the group to which the element belongs
ii an understanding that the first ionisation energy of successive elements provides evidence for electron sub-shells

i) Evidence for electron shells

The series of successive ionization energies for an element provide evidence for the existence of **electron (quantum) shells** (or energy levels) around the nucleus.

Logarithms are used to plot ionization energies because they range over several orders of magnitude.

- The first ionization energy is the lowest, because an electron in an outer shell, furthest from the nucleus, is removed first.
- The very large increase between first and second ionization energies of sodium arises because the second electron has to be removed from a shell that is closer to the nucleus.
- Electrons closer to the nucleus have fewer electron shells between them and the nucleus – they are less 'shielded' from the positive attraction of the protons.
- Electron shells closer to the nucleus are attracted towards it more strongly.



- There is a big jump between 9th and 10th ionization energies for sodium. The 10th and 11th electrons to be removed from sodium are in the shell closest to the nucleus and are very strongly attracted to it.
- You can work out which group an element is in from where the first jump is in its successive ionization energies.

Subshells

Quantum mechanics also tells you that each shell may contain a number of subshells. These subshells are described by letter: s, p, d, f.

Shell	Subshells
1	1s
2	2s, 2p
3	3s, 3p, 3d
4	4s, 4p, 4d, 4f

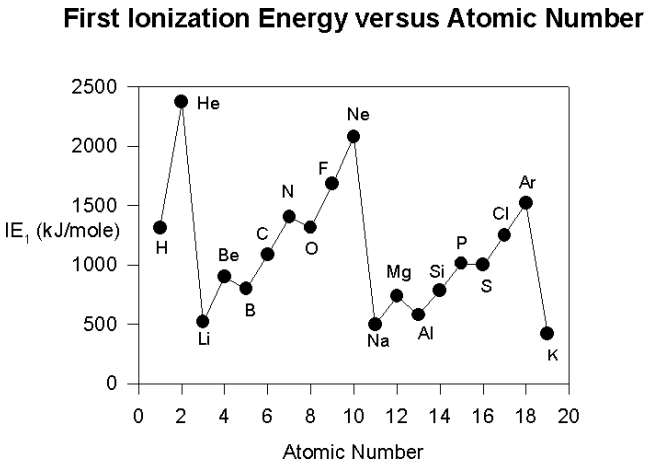
Shell 1 is closest to the nucleus so it takes the most energy to remove electrons in this shell. Within a shell the subshells have different energies, with electrons in the lowest energy subshells being closest to the nucleus:

s (lowest energy) < p < d

Each type of subshell contains one or more orbitals. An orbital is the region where the electrons are most likely to be found. An s sub-shell has one's orbital, the p sub-shell has three p orbitals and d sub-shell has five d orbitals.

ii) Evidence for electron sub-shells

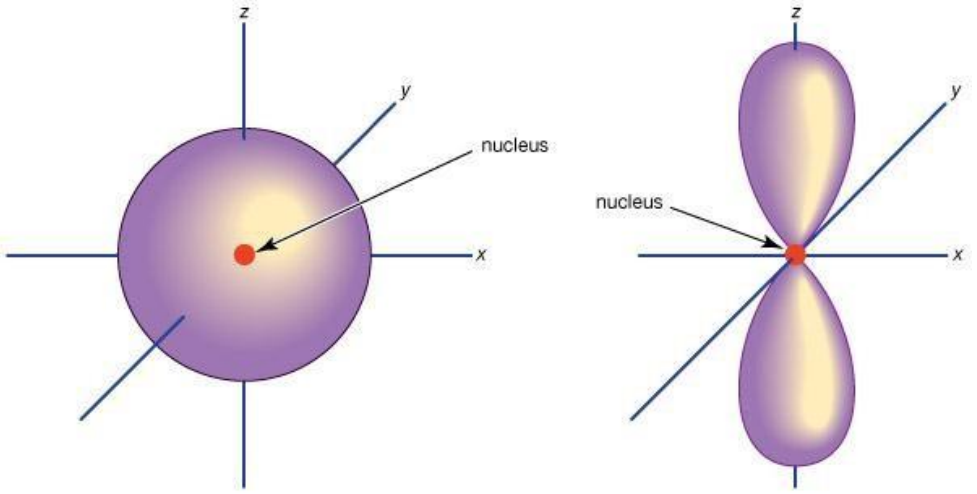
The first ionization energy of successive elements provide evidence for electron **sub-shells**. For example, removing the outer electrons from nitrogen (Z=7) involves breaking into half full p sub-shell. This requires more energy than removing the outer electron from oxygen (Z=8), which leaves a half-full sub-shell.



Generally, ionization energies increase across a period, such as from lithium (Z=3) to neon (Z=10) due to greater force of attraction between the nucleus and outer electrons. However, ionization energy decreases slightly between beryllium (Z=4) and boron (Z=5) and between nitrogen (Z=7) and oxygen (Z=8). This suggests that a given shell is divided into sub-shells that can have slightly different energies.

The reasons for the different energy levels of sub-shells within a shell can be explained by the rules for shell filling and electron pairing. *(Covered in k)*

f describe the shapes of electron density plots (or maps) for s and p orbitals



The orbitals have distinctive shapes – s orbitals are spherical, p orbitals are dumb-bell shaped.

Electron density maps of electron orbitals show how the **electron cloud** is distributed within the orbital.

All the orbitals in a given sub-shell are at the same energy level, but the 2s sub-shell is at a different energy to the 2p sub-shell.

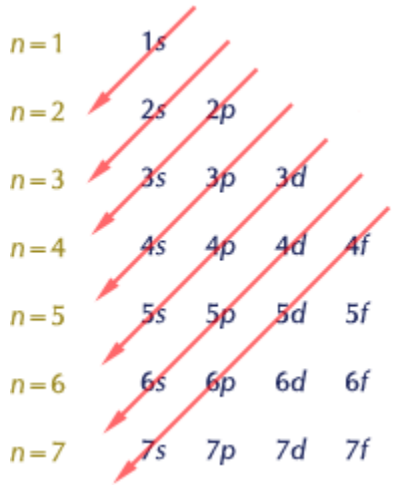
g predict the electronic structure and configuration of atoms of the elements from hydrogen to krypton inclusive using 1s …notation and electron-in-boxes notation (recall electrons populate orbits singly before pairing up)

i) Sub-shells have orbitals.

Sub-shell	**Number of orbitals**	**Maximum number of electrons in subshell**	
s	1	↑↓	=2
p	3	↑↓ ↑↓ ↑↓	=6
d	5	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	=10
f	7	↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓	=14

Each orbital can contain a maximum of two electrons (of opposite **spin**) – so each s sub-shell can hold 2 electrons, each p sub-shell 6 electrons and each d sub-shell 10 electrons. Electrons are filled in orbits singly before they pair up.

ii) Electrons will enter orbital with increasing energy.



1s 2s 2p 3s 3p 4s 3d 4p 5s 4d …

iii) There is no d^4 and d^9

Example:

Fe (26) = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^6$

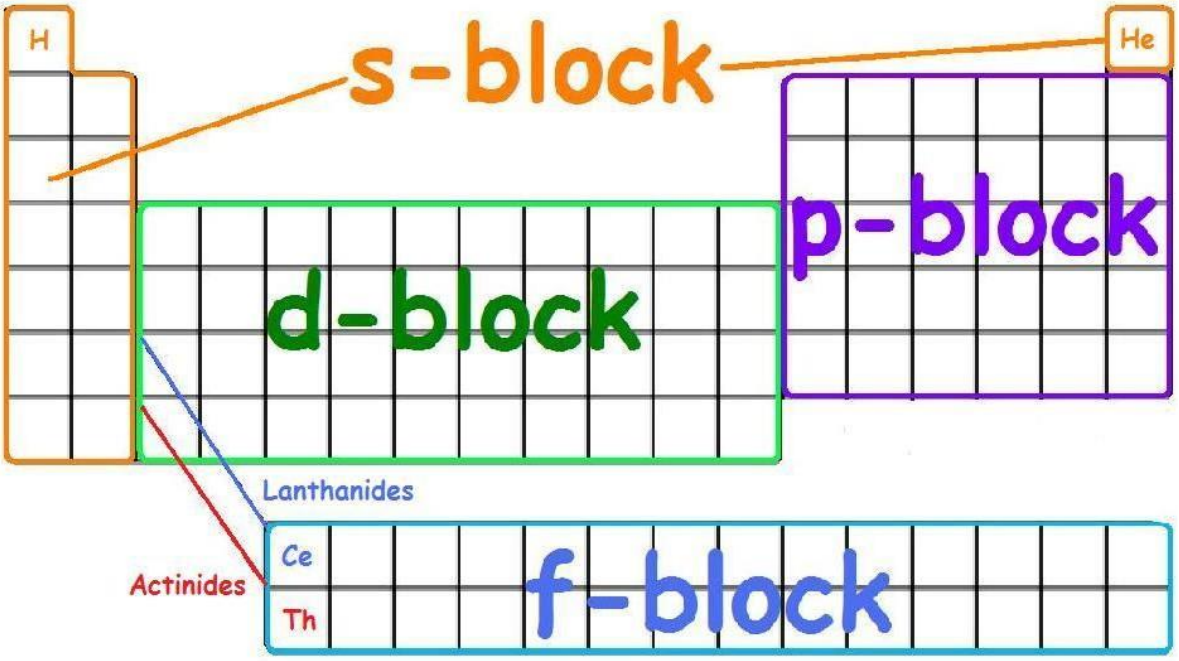
= 2,8,16,2

h demonstrate an understanding that electronic structure determines the chemical properties of an element

Elements with similar electronic configuration have similar chemical properties. E.g.: In group I elements, one electron is in their outer shell. So all the atoms of group I show similar chemical properties.

i recall that the periodic table is divided into blocks, such as s, p and d

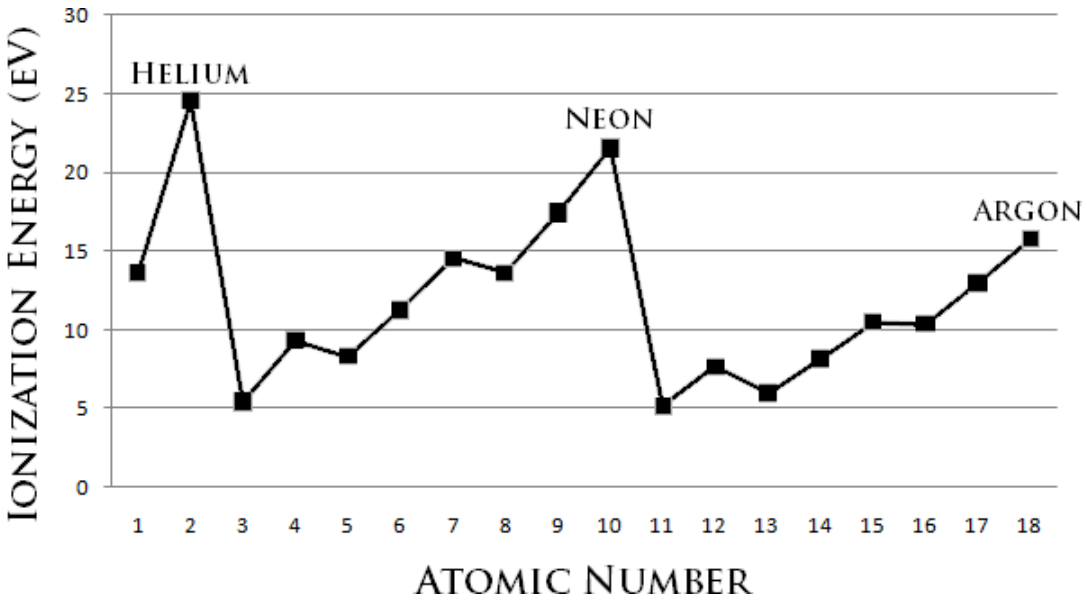
The periodic table is divided into blocks – s, p and d



s block elements have electrons in the outer shell at s orbitals. Same case with p and d.

j represent data, in a graphical form, for elements 1 to 36 and use this to explain the meaning of the term periodic property

A periodic property has a trend which repeats across periods. For example, the first ionization energy tends to increase across a period and decreases down a group.



k explain trends in the following properties of the element from periods 2 and 3 of the periodic table:
i melting temperature of the elements based on given data using the structure and the bonding between the atoms or molecules of the element
ii ionisation energy based on given data or recall of the shape of the plots of ionisation energy versus atomic number using ideas of electronic structure and the way that electron energy levels vary across the period.

(i) Melting temperature is another **periodic** property of elements.

The melting temperature of an element depends on its structure and bonding:

- metallic structures (e.g. metals in Group 1, 2 and 3) are strong – it takes a lot of energy to break the bonds that hold the atoms/ions together
- giant molecular structures (e.g. C and Si in Group 4) are held together by covalent bonds which are strong – it is very difficult to melt these elements
- simple molecular structures (e.g. S_8 and Cl_2) are held together by weak forces of attraction between the molecules – it requires little energy to overcome these intermolecular forces of attraction, the melting temperatures are low.

Melting temperature rise from Group 1 to Group 2 to Group 3 because the number of shared delocalized electrons increases, which increases the metal bonding.

(ii) The first ionization energy of an element is directly related to the attraction of the nucleus for the most loosely bound of the outer electrons. The more tightly held the outer electrons,

the higher the first ionization energy. There are three main factors that affect the ionization energy of an atom:

- *The attraction between the nucleus and the outermost electron* – decreases (reducing the ionization energy) as the distance between them increases.
- *The size of the positive charge* – a more positive nucleus has a greater attraction for the outer electron, leading to a higher ionization energy.
- *Inner shells of electrons repel the outer electron, screening or shielding it from the nucleus* – the more electron shells there are between the outer electron and the nucleus, the less firmly held is the outer electron and the lower will be the ionisation energy.

Ionisation energy increases across a period – it becomes harder to remove an electron. This is the result of increasing positive nuclear charge across the period without the addition of any extra electron shells to screen the outer electrons. The atomic radius gets smaller and the electrons are held more firmly, so it requires more energy to bring about ionisation. The end of each period is marked by the high energy of a noble gas which is a result of their stable electronic structure and unreactive nature.

However, the ionisation energy does not increase smoothly across a period. This is due to the presence of sub-shells within each shell. For example, the ionisation energy of aluminium is less than magnesium. Because removing one electron from aluminium removes the single electron in the p subshell. But for magnesium, an electron must be removed from a full s subshell. Full subshells are particularly stable and requires more energy than removing the single p electron from aluminium.

The unexpectedly high first ionisation energies of nitrogen and phosphorus can be explained by the fact that both these elements contain half-full outer p subshells with greater stability. Removing an electron from an atom of oxygen or sulfur removes the fourth electron in p subshell, leaving a half-full p subshell. On the other hand, removing one electron from a nitrogen or phosphorus atom requires breaking into a half-full subshell, a process that requires more energy. Successive ionisation energies like those provide clear evidence for the existence of energy shells and subshells in the structure of the atom.

Ionisation energy generally decreases down a group. The outer electron is increasingly further from the nucleus and electron shielding by the additional inner shells reduces the attraction to the nucleus – it becomes easier to remove it from the atom.

Topic 3: Bonding and Structure

1 Ionic Bonding

a recall and interpret evidence for the existence of ions, limited to physical properties of ionic compounds, electron density maps and the migration of ions, e.g. electrolysis of aqueous copper chromate(VI)

The evidence that ions exist

- **Physical properties** of ionic compounds: high melting temperatures, showing strong forces of attraction between ions, soluble in polar solvents, conduct electricity when molten or in aqueous solution.
- **Electron density maps**. When x-ray are passed through an ionic crystal onto photographic film. They are diffracted by the electrons an produce bright spots on the film. The bigger the ion the more electrons it has and the brighter the spot it produces. This diffraction show zero electron density between ions – meaning complete electron transfer.
- Migration of ions in **electrolysis**. For example, electrolysis of green aqueous copper (II) chromate (VI) attracts a yellow colour (chromate (VI) ions) to the anode and a blue colour (copper (II) ions) to the cathode.

b describe the formation of ions in terms of electron loss or gain

An ion is formed when an atom gains or loses one or more electrons. For example, a copper atom loses two electrons:

$$Cu\ (g) \rightarrow Cu^{2+}\ (g) + 2e^-$$

to form a copper **cation**. A chlorine atom gains one electron:

$$Cl\ (g) + e^- \rightarrow Cl^-\ (g)$$

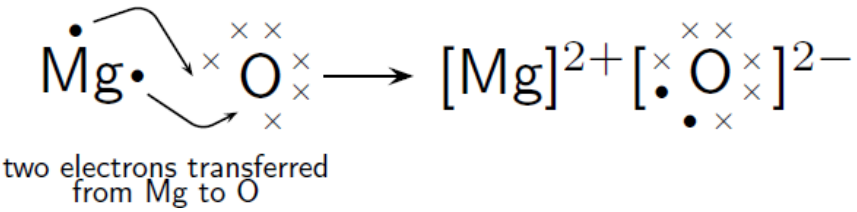
to form a chloride **anion**.

- A positive ion is called a **cation**, it is attracted towards the cathode in electrolysis.
- A negative ion is called an **anion**, it is attracted towards the anode in electrolysis.

When ions are formed they tend to have a fuller outer shell, i.e. eight electrons. This is called **octet rule**. Ions with full outer shells have the same electronic configuration as noble gases (Group 0) – for example, a Ca^{2+} ion has the same electronic configuration as argon; they are **isoelectronic**.

c draw electron configuration diagrams of cations and anions using dots or crosses to represent electrons

Ionic bonding between Magnesium and Oxide



d describe ionic crystals as giant lattices of ions

- In **ionic compounds** each ions is surrounded by ions of the opposite charge. eg. Each sodium ions is surrounded by 6 chlorine ion and each chloride ions are surrounded by 6 sodium ions.
- Ionic compounds form **giant ionic lattice** in the solid state (also called an ionic crystal).

e describe ionic bonding as the result of strong net electrostatic attraction between ions

Ionic bonding can be thought of as the net electrostatic attraction between the ions. As ion attract ions with the opposite charge and repels ions with same charge. The lattice structure of a particular ionic compound is simply the arrangement of ions in a way that maximizes the attractive forces between the oppositely charged ions and minimizes the repulsion between similarly charged ions. The forces exerted by the ions in a giant lattice act equally in all directions, holding the ions together tightly.

An **ionic bond** is an omnidirectional **electrostatic force** of attraction between oppositely charged ions.

- The forces of attraction are equal in all directions.

f recall trends in ionic radii down a group and for a set of isoelectronic ions, e.g. N^{3-} to Al^{3+}

The **ionic radius** is the radius of an ion in its crystal form.

- Cations are smaller than the original atom since the atom loses electrons. Usually a whole electron shell has been lost, and the remaining electrons are also pulled in towards the nucleus more strongly.
- Anions are larger than the original atoms since the atom gains electrons and there is more repulsion in the electron cloud.

Going down a group in the Periodic table, the ions become larger – the number of shells is increasing.

Isoelectronic ions have different ionic radii:

- the additional electrons in anions make the ions larger because there is a greater repulsion and the electrons are less tightly bound than in the atom
- the loss of electrons to form cations means the nucleus attracts those electrons that remain more strongly. For example, for the electronic configuration $1s^2 2s^2 2p^6$, the order size is
  $N^{3-} > O^{2-} > F^- > Ne > Na^+ > Mg^{2+} > Al^{3+}$

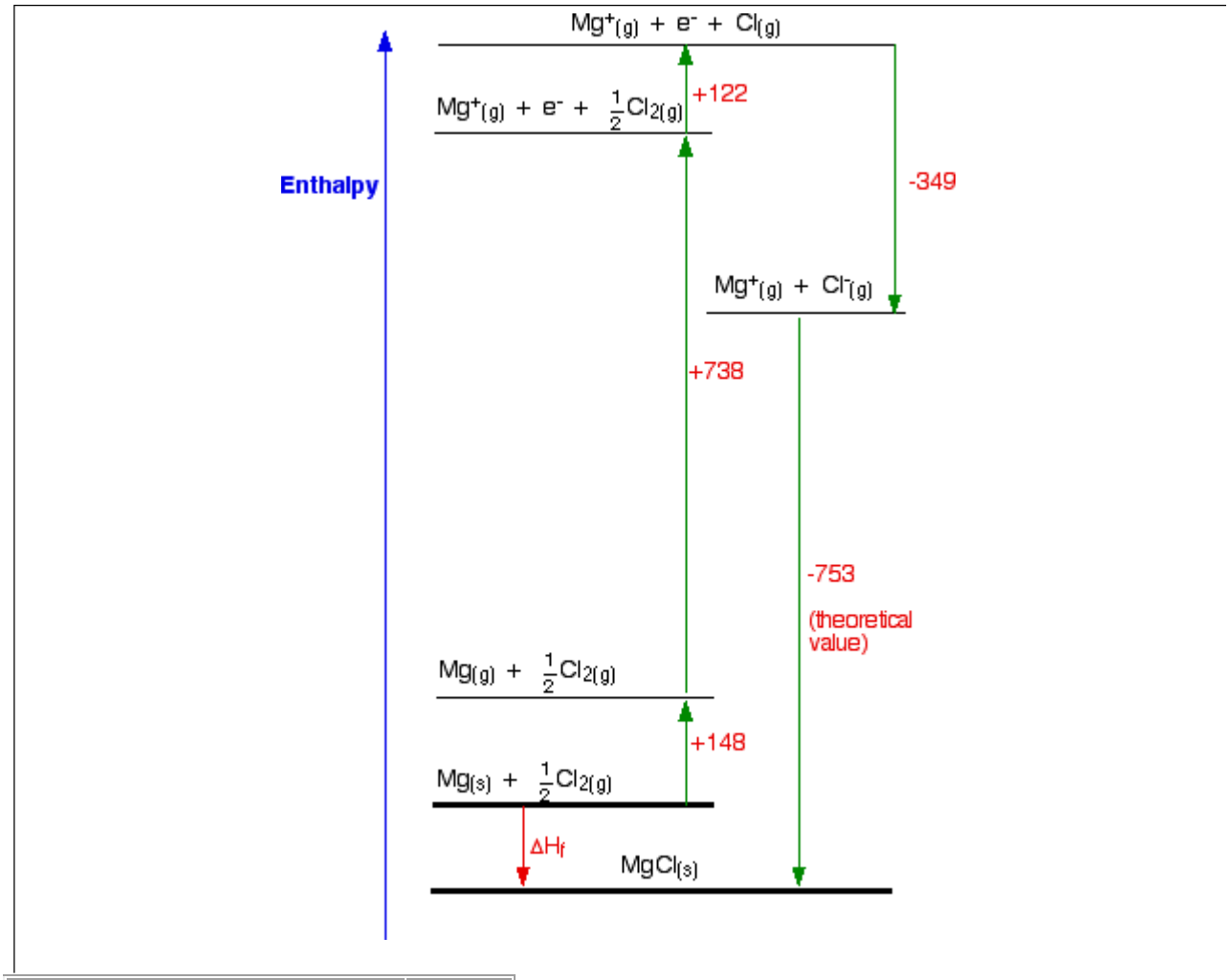
g recall the stages involved in the formation of a solid ionic crystal from its elements and that this leads to a measure value for the lattice energy (students will not be expected to draw the full Born-Haber cycles)

The formation of ionic crystal from its elements is exothermic. The **lattice energy** is the energy released when 1 mole of an ionic crystal is formed from its ions in the gaseous state, under standard conditions. This process can be broken down into a number of stages, each associated with a particular energy change:

- atomization of the metal
- ionization of the gaseous metal
- atomization of the non-metal
- ionization of gaseous non-metal atoms (called the electron affinity)
- forming the crystal from the gaseous ions.

The lattice energies of substances can be calculated from a special type of enthalpy level diagram called a **Born-Haber cycle**.

Calculate the formation enthalpy of MgCl.



	kJ
atomisation enthalpy of Mg	+148
1st IE of Mg	+738
atomisation enthalpy of Cl	+122
electron affinity of Cl	-349
lattice enthalpy	-753
calculated ΔH_f	-94

ΔH_f = +148 + 738 + 122 - 349 - 753

ΔH_f = -94 kJ mol-1

Factors affecting lattice energy

The size of the lattice energy of a compound is affected by both charge and size of the ion. The lattice energy becomes more exothermic as the size of ion decreases and the charge of the ions increases. With smaller ions the attractive force of the positive nucleus hold the outer electron more tightly because they are more closer to the nucleus, as a result of this more energy would be needed to break them apart.

h test the ionic model for ionic bonding of a particular compound by comparison of lattice energies obtained from the experimental values used in Born-Haber cycles, with provided values calculated from electrostatic theory

The Born-Haber cycle users measured enthalpies to calculate lattice energies. Lattice energy can also be calculated from a model using Coulomb's law (electrostatic attraction), assuming complete electron transfer in ionic compounds, and the size of the ionic radii. Coulomb's law calculates the force of attraction between ions as a function of their charges and the distance between them.

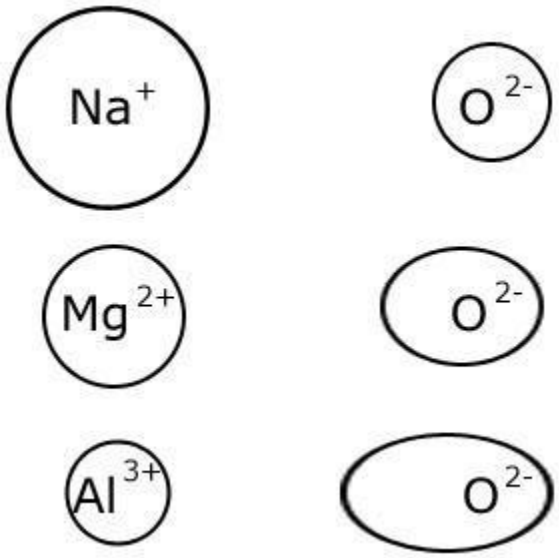
This ionic model can be tested for different compounds by comparing experimental (Born-Haber) results with theoretical results from the model.

Compound	**Lattice energy/kJ mol^{-1}**	
	Born-Haber	**Theoritical**
NaF	918	912
NaCl	780	770
NaBr	742	735
NaI	705	687
AgF	958	920
AgCl	905	883
AgBr	891	816
AgI	889	778

i explain the meaning of the term polarisation as applied to ions

Polarization of an ion is the distortion of its electron cloud away from completely spherical:

- a cation will distort an anion
- a cation has **polarizing power**
- an anion is **polarizable**



j demonstrate an understanding that the polarising power of a cation depends on its radius and charge, and the polarisability of an anion depends on its size

The **polarizing power** of cation depends on its charge density:

- a small cation is more polarizing than a larger one – the positive nucleus has more effect across the small ionic radius
- a cation with a large charge is more polarizing than one with a small charge – a large charge has more attraction than a small one

The **polarizability** of an anion depends on its size alone:

- a large anion is easily polarized – its electron cloud is further from the nucleus and is held less tightly than on a smaller anion.

k demonstrate an understanding that polarisation of anions by cations leads to some covalency in an ionic bond, based on evidence from the Born-Haber cycle

The different methods of obtaining the lattice energies (see h) for the sodium halides produce very similar results. But this is not the case for the silver halides – their lattice energies are more exothermic (more negative and more stable) then theory would predict.

- Coulomb's law assumes that the ions are completely separate and spherical (not distorted).
- Experiment therefore suggests that there is a degree of electron sharing, i.e. covalency, in the silver halides, while the sodium halides show (almost) pure ionic bonding.

This is supported by lower melting temperatures for silver halides than sodium halides.

I use values calculated for standard heats of formation based on Born-Haber cycles to explain why particular ionic compounds exist, e.g. the relative stability of $MgCl_2$ over MgCl or $MgCl_3$ and NaCl over $NaCl_2$.

Born-Haber cycle can be used to predict the relative stabilites of ionic compounds, and even if a particular formula will exist as a compound.

Why is calcium chloride $CaCl_2$, and not CaCl or $CaCl_3$?

The theoretical enthalpy change of formation for each compound is found by adding the energies in each of the columns. Using the data, the enthalpy changes of formation for the three compounds are:

- $Ca(s) + \frac{1}{2} Cl_2(g) \rightarrow CaCl(s)$ $\quad \Delta H_f^{\ominus} = -170$ kJ/mol
- $Ca(s) + Cl_2(g) \rightarrow CaCl_2(s)$ $\quad \Delta H^{\ominus} = -796$ kJ/mol
- $Ca(s) + \frac{3}{2} Cl_2 \rightarrow CaCl_3(s)$ $\quad \Delta H_f^{\ominus} = +1341$ kJ/mol

The most stable compound is that with the most exothermic enthalpy of formation, $CaCl_2(s)$. The formation of $CaCl_3$ is highly endothermic, because the very high 3rd ionization enthalpy cannot be provided by the extra lattice energy. The reason for the high 3rd ionization energy lies that the third ionisation involves breaking into a noble gas configuration.

2 Covalent Bonding

a demonstrate an understanding that covalent bonding is strong and arises from the electrostatic attraction between the nucleus and the electrons which are between the nuclei, based on the evidence:
i the physical properties of giant atomic structures
ii electron density maps for simple molecules

Formation of covalent bonds

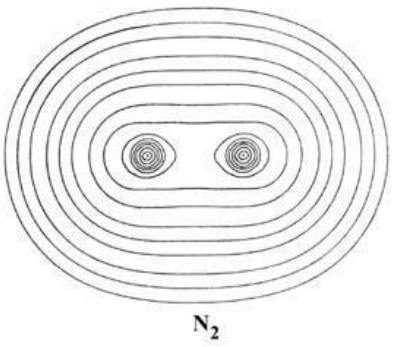
A **covalent bond** is formed when a pair of electrons is shared between two atoms. This happens when two atoms approach each other and their electron clouds overlap and electron density is greatest between the nuclei. This region of high electron density (the covalent bond) attracts each nucleus and therefore keeps the atoms together.

- Covalent bonding is a strong electrostatic attraction between the nuclei of the bonded atoms and the **shared pair of electrons** between them.
- The distance between the two nuclei is the **bond length**. It is the separation at which the energy of the system is at its lowest.

The evidence of covalent bonds

The physical properties of **giant atomic structure** such as diamond provide evidence for the strong electrostatic attraction in covalent bonding. Giant atomic structures are also known as **giant molecular structures**. They are very hard and have high melting temperatures. The covalent bonds are very strong, holding the atoms in place and require a lot of energy to break them before the atoms can move in a liquid.

Electron density maps show high electron density between atoms that are covalently bonded.



Electron density in covalent bonds between two nitrogen atoms showing region of high electron density between two atoms.

b draw electron configuration diagrams for simple covalently bonded molecules, including those with multiple bonds and dative covalent bonds, using dots or crosses to represent electrons.

Dative covalent bonds are formed when both the shared electrons come from just one of the atoms.

For example, aluminium chloride, $AlCl_3$, will form dimers (a combination of two identical molecules) of Al_2Cl_6. The aluminium atom in aluminium chloride is electron-deficient (only six electrons in its outer shell) but by forming dative covalent bonds the **octet rule** is fulfilled.

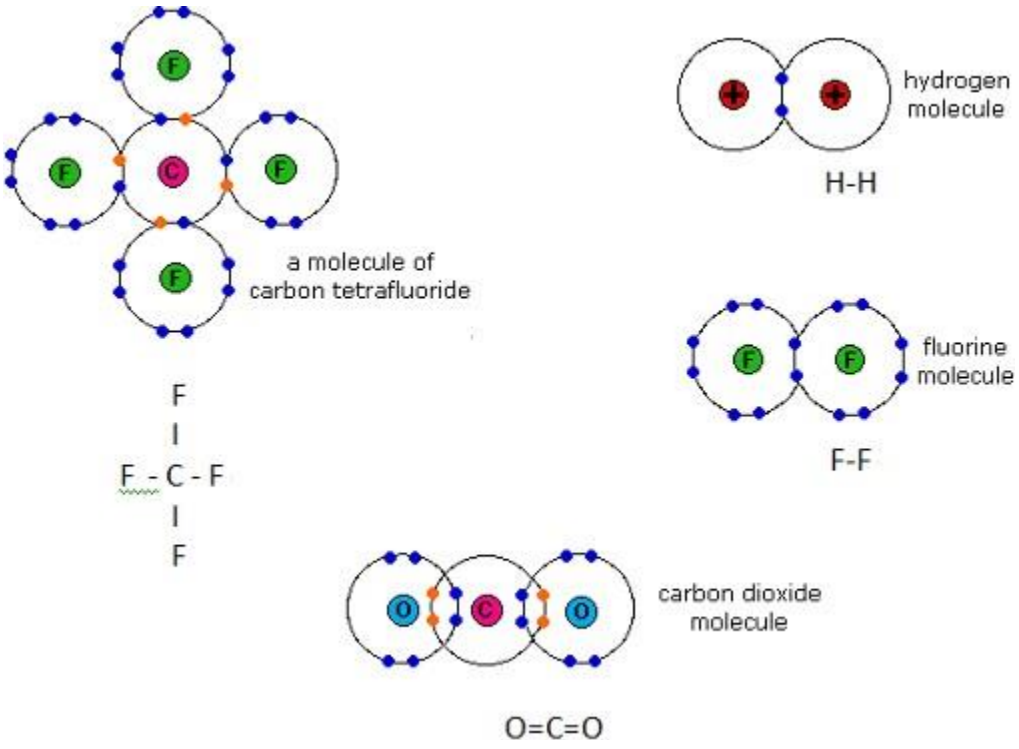
Atoms can share more than one pair of electrons and form double or triple covalent bonds:

- a **double bond** results from two shared electron pairs – e.g. in oxygen, O_2
- a **triple bond** results from three shared electron pairs – e.g. in nitrogen, N_2

Covalent dot – and – cross diagrams

Only electrons in the outer shell are shown in these diagrams:

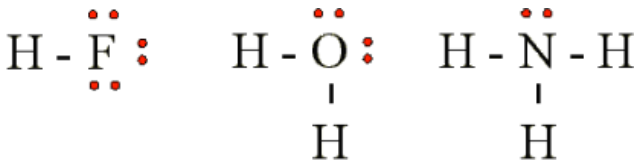
- electron pairs are drawn at four points
- electrons are paired between atoms to form outer shells of eight electrons (two for hydrogen)
- the electrons from one type of atom are usually shown with crosses and those from the other atoms with dots.



Lone pairs

In some molecules not all the electrons in the outer shell may be involved in bonding.

- A non-bonding pair of electrons is called **lone-pair.**
- Lone pairs are shown on dot-and-cross diagrams on one atom only (not shared).
- Lone pairs affect the shape of molecules.



3 Metallic Bonding

a demonstrate an understanding that metals consist of giant lattices of metal ions in a sea of delocalised electrons

Metals consist of **giant lattices** of metals ions in a seo of **delocalized electrons**. The metal ions vibrate about fixed points in the solid lattice, being held in place by the electrons (also vibrating) around them. It is the **outer electrons** of the metal that have become **delocalized** – they no longer associated with one particular atom.

b describe metallic bonding as the strong attraction between metal ions and the sea of delocalised electrons

Metallic bonding is the strong attraction between metals ions and the sea of delocalized elctrons.

c use the models in 1.6.3a and 1.6.3b to interpret simple properties of metals, e.g. conductivity and melting temperatures.

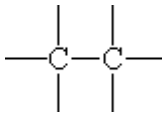
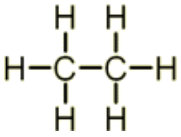
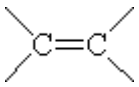
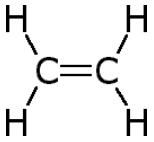
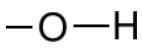
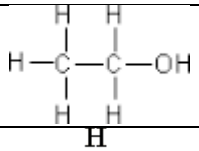
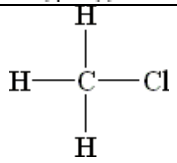
The typical characteristics of metals can be explained using this simple model of metallic bonding.

- **Electrical conductivity**: the delocalized electrons are free to move in the same direction when an electric field is applied to the metal; the movement of charged particles is an electric current.
- **Thermal conductivity**: the delocalized electrons transmit kinetic energy (heat) through the metal, from a hot region to a cooler one, by colliding with each other.
- **High melting temperatures**: the positive ions are strongly held together by the attraction of the delocalized electrons; it takes a lot of energy to break the metallic bonds and allow the particles to move around in the liquid state.
- **Malleability and ductility**: metals can be hammered into shape (malleable) or stretched into wire (ductile) because the layers of the positive ions can be forced to slide across each other while staying surrounded by the sea of delocalized electrons.

1 Introduction

a demonstrate an understanding that there are series of organic compounds characterised by a general formula and one or more functional groups

There are series of **organic compounds** which are called **homologous series** and each homologous series has a **general formula** and one or more **functional groups** that determines the properties of that series.

Homologous series	General formula	Functional group	Example: structural formula	Example: displayed formula
Alkanes	C_nH_{2n+2}		Ethane CH_3CH_3	
Alkenes	C_nH_{2n}		Ethene CH_2CH_2	
Alcohols	$C_nH_{2n+2}O$		Ethanol C_2H_5OH	
Halogenoalkanes	$C_nH_{2n-1}X$	- X	Chloromethane CH_3Cl	

b apply the rules of IUPAC nomenclature to compounds relevant to this specification and draw these compounds, as they are encountered in the specification, using structural, displayed and skeletal formulae

IUPAC's rules of **systematic name** of organic compound include:

1. the number of carbon atoms in the molecule
2. the homologous series to which it belongs
3. whether the molecule is a straight or branched chain or a ring
4. the names of any other atoms in the compound

1. The prefix of the name gives the number of carbon atoms in the longest chain – e.g. methane, CH_4, has 1 carbon atom and pentane has 5.

Prefix	**Number of carbon atoms in the main carbon chain**
meth-	1
eth-	2
prop-	3
but-	4
pent-	5
hex-	6
hept-	7
oct-	8
non-	9
dec-	10

2. The suffix of the name gives the type of compound – the homologous series to which it belongs. For example, methanol, CH_3OH, is an alcohol, pentene is an alkene and ethanol is an aldehyde.

Suffix	**Homologous series**
-ane	alk**ane**
-ene	alk**ene**
-ol	alcoh**ol**
-oic	carboxyl**ic** acid
-al	**al**dehyde
-one	ket**one**

3. When branches, functional groups and carbon-carbon multiple bonds are located, we use numbers in the names:

- The numbers refer to the carbon atoms in the longest chain to which any functional group (including multiple bonds and side-chains) is attached.
- The longest carbon chain is numbered from the end that will give the lowest numbers.

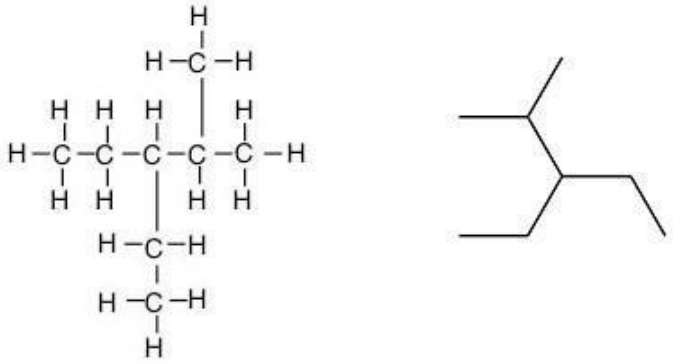
4. Alkyl groups are branches. These are alkane molecules that have lost a hydrogen atom – e.g. the ethyl group comes from ethane

The first three alkyl groups are:

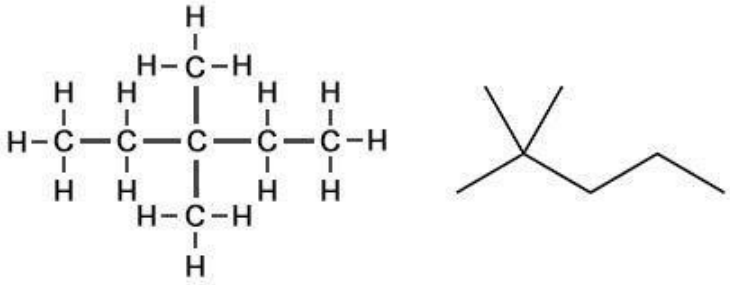
- methyl CH_3 –
- ethyl C_2H_5 –

- propyl C_3H_7 –

Multiple side chains or functional groups are listed in alphabetical order. If two functional groups are attached to the same carbon atom then the number of that atom is repeated. If repeated functional groups are the same then the name contains di, which becomes tri for three and tetra for four.



3-ethyl-2-methylpentane



2,2-dimethylpentane

Skeletal formula: A skeletal formula is a simplified organic formula. It shows the bonds in the carbon skeleton and any functional groups, with hydrogen atoms removed from alkyl chains. You need to be able to use skeletal formulae, so these have been included with displayed formulae for you to recognise. The ends of the lines or junctions represent carbon atoms, and hydrogen atoms take up any unused carbon bonds.

c appreciate the difference between hazard and risk

Hazard: The potential of a substance to do harm. This is absolute. E.g. petrol is toxic and flammable.

Risk: Risk is the change of a substance that will cause harm. This is variable. E.g. filling a car with petrol carries a low risk of harm due to the safety precautions which are in place, but lightning a fire using petrol is very dangerous since the invisible petrol vapour is not under control.

d demonstrate an understanding of the hazards associated with organic compounds and why it is necessary to carry out risk assessments when dealing with potentially hazardous materials. Suggest ways by which risks can be reduced and reactions can be carried out safely by:

i working on a smaller scale
ii taking specific precautions or using alternative techniques depending on the properties of the substances involved
iii carrying out the reaction using an alternative method that involves less hazardous substances.

Types of hazard

Organic chemicals present a range of different hazards. Their containers, transport boxes, storage bottles, lab bottles etc. carry hazard symbols. Different hazards require different precautions to be taken:

- **flammable** materials need to be kept away from ignition sources
- **corrosive** materials should be prevented from getting on your skin
- **toxic** materials must not be allowed into the body either through skin proportion or inhalation
- **oxidizing** materials have to be carefully used with fuels or reducing agents.

Reducing risk

The total elimination of risk, while continuing with the normal functioning of society, is almost impossible – e.g. crossing a road without risk is impossible.

A **risk assessment** identifies the hazards involved in an activity. It is used to reduce the risk of harm to as low as reasonably possible. Any activity or reaction undertaken in a lab requires a risk assessment to have been done before it is carried out. A risk assessment will involve the following steps:

1. Identifying the hazards associated with the chemicals and procedures involved.
2. Quantifying the risks by considering, for example, the amount of substances to be used, where the procedure will be done and the experience of the people involved.
3. Identifying who is at risk.
4. Stating the controls used to minimize the risk – e.g. use a fume cupboard.

5. Making a decision as to whether the risk is at an acceptable level for the activity to proceed.

Risk can be reduced by:

- Using less material – the reaction is easier to contain and to control, and the risk of spillage is reduced.
- Using lower concentrations of solutions – diluted **corrosive** solutions can become **irritants**, still a hazard but a much reduced one.
- Using an electric heating mantle instead of naked flame of a Bunsen burner to heat flammable liquids or solutions.
- Using specific protective clothing – e.g. gloves when handling corrosive liquids.
- Doing a reaction in a fume cupboard – thus removing harmful vapours from the work area.
- Reducing the temperature at which the procedure is carried out – thus slowing the reaction and reducing the risk of overheating and too many fumes being produced.
- Changing the materials used – less hazardous compounds may not react as quickly or give as much product, but they will still allow the same reaction to be studied.
- Having assessed the hazards and applied risk assessments, laboratories are very safe place to work – often saver than everyday life!

2 Alkanes

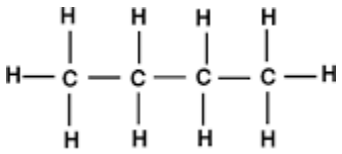
a state the general formula of alkanes and understand that they are saturated hydrocarbons which contain single bonds only

Alkanes general formula is C_nH_{2n+2}. They only contain carbon-carbon single bonds and therefore called saturated hydrocarbons.

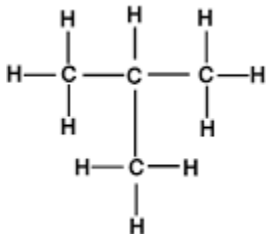
b explain the existence of structural isomers using alkanes (up to C_5) as examples

Isomers are the compounds with same molecular formula but with different structures. e.g

n – Butane



2 – methylpropane



Physical property may vary due to different isomers. The boiling point of branch-chain isomer is lower than the long chain isomer.

c know that alkanes are used as fuels and obtained from the fractional distillation, cracking and reformation of crude oil

Alkanes are used as **fuels**. They burn in excess oxygen to produce carbon dioxide and water only.

Obtaining alkane:

The source of alkane is fossil fuel or commonly known as crude oil or petroleum. Once they have been extracted it undergoes fractional distillation.

Crude oil is pre-heated and then injected to fractionating tower. The tower is designed as hotter at the bottom and cooler at the top. Now crude oil converts to vapour and rises up the fractionating tower as it is a mixture of different hydrocarbons, different fraction of molecules will be obtained. As these fragment rises up the tower, the temperature when settles down to its boiling temperature, the fragments condenses to liquid and is collected.

Fragments from crude oil

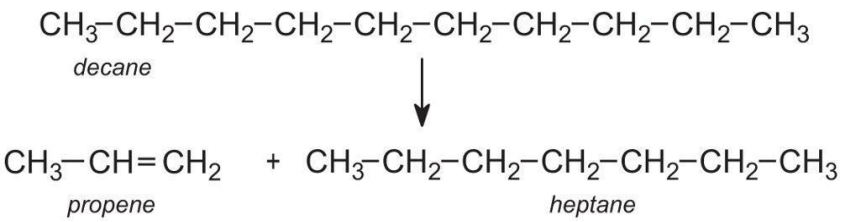
- 1-2% of refinery gas mainly containing gaseous alkanes starting from carbon-1 to carbon-4. These mainly used for domestic heating.
- 15-30% of gasoline. It contains mixture of liquid hydrocarbon ranging from carbon-5 to carbon-10. These are widely used as fuel for internal combustion engines that powers car.
- 10-15% of kerosene. These are mainly liquid hydrocarbon in between carbon-11 and carbon-12. They are mainly used as fuel for aircraft engine.
- 15-20% of diesel oil/ gas oil. They are mainly mixture ranging from carbon-13 to carbon-38 and are mainly used as fuel for industrial boilers.
- 40-50% residue. These are very complex mixture of hydrocarbons with high viscosity and high boiling temperature it can be used as fuel for, furnaces from power station and some is mixed with rod chippings for road surfacing.

Cracking

Cracking is the name given to breaking up large hydrocarbon molecules into smaller and more useful bits. This is achieved by using high pressures and temperatures without a catalyst, or lower temperatures and pressures in the presence of a catalyst.

Temperature: 700 – 800 °C
Catalyst: Alumina (Al_2O_3)

Example:



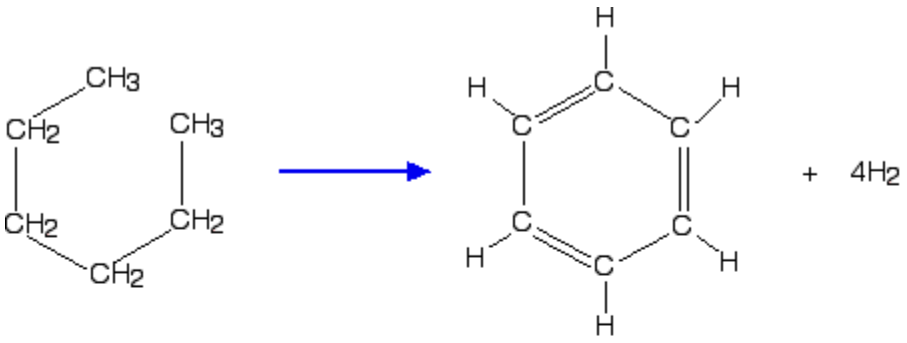
Reforming

Reforming is another process used to improve the octane rating of hydrocarbons to be used in petrol, but is also a useful source of aromatic compounds for the chemical industry. Aromatic compounds are ones based on a benzene ring.

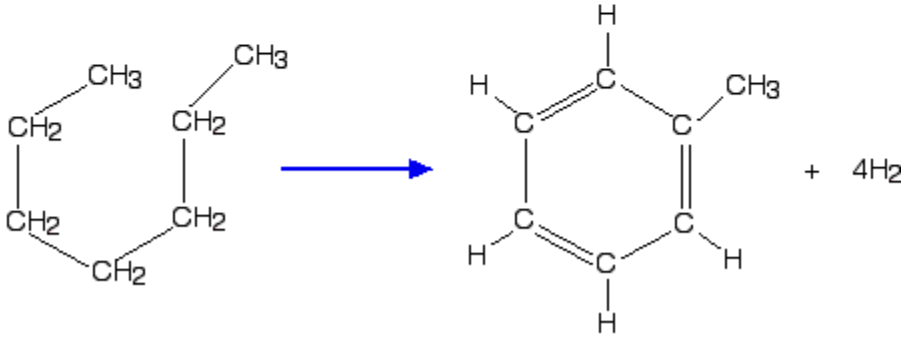
A hydrocarbon with a high octane rating burns more smoothly than one with a low octane rating. Molecules with "straight chains" have a tendency to pre-ignition. When the petrol / air mixture is compressed they tend to explode, and then explode a second time when the spark is passed through them. This double explosion produces knocking in the engine.

Reforming uses a platinum catalyst suspended on aluminium oxide together with various promoters to make the catalyst more efficient. The original molecules are passed as vapours over the solid catalyst at a temperature of about 500°C.

Isomerisation reactions occur but, in addition, chain molecules get converted into rings with the loss of hydrogen. Hexane, for example, gets converted into benzene, and heptane into methylbenzene.



hexane benzene



heptane methylbenzene

d discuss the reasons for developing alternative fuels in terms of sustainability and reducing emissions, including the emission of CO2 and its relationship to climate change

The crude oil from which fuels can be derived is not a sustainable resource. Because the increased numbers of vehicles are increasing the amount of carbon dioxide emissions from burning traditional fuels. This is thought to be causing global warming.

Therefore, alternative fuels are being developed to try to reduce greenhouse gas emissions and to increase sustainability.

Hydrogen has been considered as an alternative fuel to hydrocarbons. It burns to make water only – this is very 'clean', but H_2O is a greenhouse gas. It also combines with oxygen in fuel cells to generate electricity, again producing only water. However, the energy used in producing hydrogen (from electrolysis of brine or reaction of methane with steam) and pressurizing the hydrogen comes from power plants that produce greenhouse gases such as carbon dioxide. Moreover, the carbon in methane is also converted to carbon dioxide during the manufacture of hydrogen – hydrogen may not be as 'carbon-neutral' as people like to think.

Biofuels, such as bioethanol and biodiesel, are becoming more available as alternatives to fossil fuels. The plants that we used to make them absorb carbon dioxide from the atmosphere as

they grow and then release it when the biofuel is burned. Not accounting for the energy requirements of the manufacturing process, biofuels are more carbon neutral than coal, oil and gas.

e describe the reactions of alkanes in terms of combustion and substitution by chlorine showing the mechanism of free radical substitution in terms of initiation, propagation and termination and using curly half-arrows in the mechanism to show the formation of free radicals in the initiation step using a single dot to represent the unpaired electron.

Combustion

Alkanes burn in excess oxygen to produce carbon dioxide and water only – for example:

- methane, the main constituent of natural gas, used to heat many homes
  CH_4 (g) + $2O_2$ (g) → CO_2 (g) + $2H_2O$ (g)
- octane, present in motor fuel, burns according to
  C_8H_{18} (l) + 12 ½ O_2 (g) → 8 CO_2 (g) + $9H_2O$ (g)

When burned in plenty of oxygen, alkanes are clean fuels. When burned in a limited supply of oxygen, alkanes undergo incomplete combustion and form carbon monoxide. This is very dangerous – it is gaseous, odourless, invisible and toxic – it can be fatal.

Incomplete combustion of alkanes can occur in:

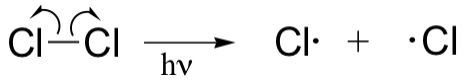
- poorly ventilated rooms
  CH_4 (g) + 1 ½ O_2 (g) → CO (g) + $2H_2O$ (g)
- and in car engines
  C_8H_{18} (l) + 8 ½ O_2 (g) → 8CO (g) + $9H_2O$ (g)

Substitution

A substitution reaction is a replacement reaction. For example, hydrogen in an alkane can be replaced by a different atom or group. Chlorine will substitute hydrogen in methane to form a halogenoalkane:

$$CH_4 (g) + Cl_2 (g) \rightarrow CH_3Cl (g) + HCl (g)$$

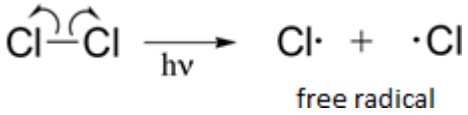
This is called **free-radical substitution**. A **radical** is a species with an unpaired electron, such Cl• formed from the dissociation of chlorine:



Alkanes undergo substitution by halogens at about 300°C or in ultraviolet light. The substitution reaction happens in steps. The sequence of steps is shown in the **reaction mechanism**.

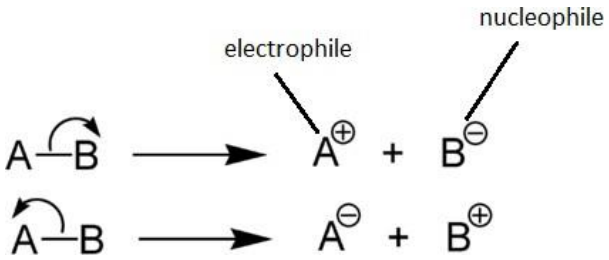
There are two types of process for bond breaking:

- Homolytic fission



  The species which is formed by hemolytic fission with an unpaired electron is called free radical. A free radical is very short lived and highly reactive.

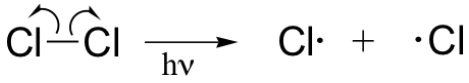
- Heterolytic fission



  During the heterolytic fission, nucleophile and electrophile is produced. Nucleophile are species having electron rich center and negative ion. Electrophile are species with electron deficient center or positive ion.

Mechanism of free-radical substitution of chlorine

Step 1: **Initiation** – Light provides the energy to split the chlorine molecules into atoms and therefore initiate the reaction. The splitting of the chlorine molecules is an example of hemolytic fission – the chlorine atoms formed are free radicals, and so are extremely reactive.



Initiation will keep going so long as there are chlorine molecules in the gas mixture.

Step 2: **Propagation** – Chlorine free radicals react with methane molecules, combining with one of the hydrogen atoms to form hydrogen chloride and another free radical:

$CH_4 + Cl^{\bullet} \rightarrow CH_3^{\bullet} + HCl$

The methyl free radical then reacts with another chlorine molecule to form chloromethane and a chlorine free radical:

$CH_3^{\bullet} + Cl_2 \rightarrow CH_3Cl + Cl^{\bullet}$

The process is then repeated hundreds of times in these propagation reaction that produce another free radical. This rapid and repeated propagation result in a chain reaction, an explosive process.

Propagation maintains the concentration of chlorine – free radicals in the gas mixture.

Step 3: **Termination** – The propagating steps of this reaction continue until there is a termination step. This is a reaction between two free radicals – a highly exothermic process. A termination step happens every few thousand reactions!

$Cl^{\bullet} + Cl^{\bullet} \rightarrow Cl_2$
$CH_3^{\bullet} + Cl^{\bullet} \rightarrow CH_3Cl$
$CH_3^{\bullet} + CH_3^{\bullet} \rightarrow C_2H_6$

Termination removes radicals from the gas mixture, thus stopping the reaction.

3 Alkenes

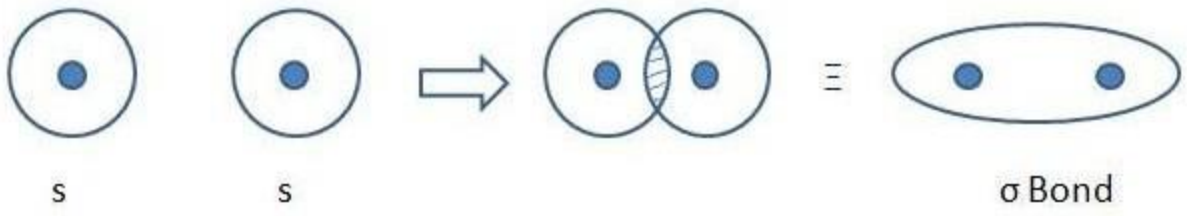
a state the general formula of alkenes and understand that they are unsaturated hydrocarbons with a carbon-carbon double bond which consists of a σ and a π bond

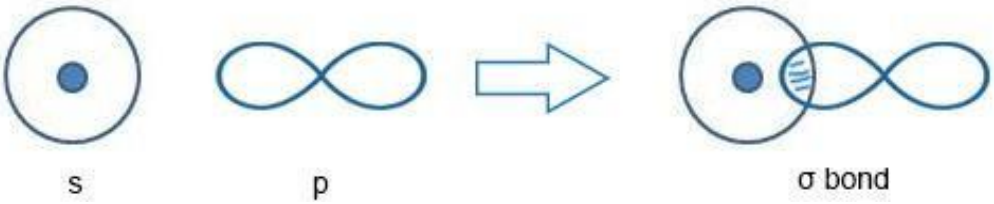
Alkenes are unsaturated hydrocarbons – they contain carbon – carbon double bonds (C = C). The general formula of the alkenes with one C = C bond is C_nH_{2n}. The alkenes form an homologous series.

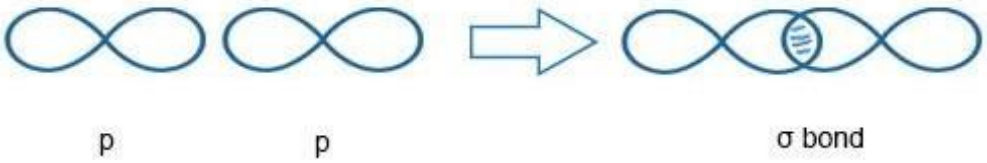
The C = C bond consists of two parts: a **σ (sigma)** bond and **π (pi)** bond.

<u>σ bond</u>

When two orbitals overlap in frontier way, then the bond which is formed is σ bond.

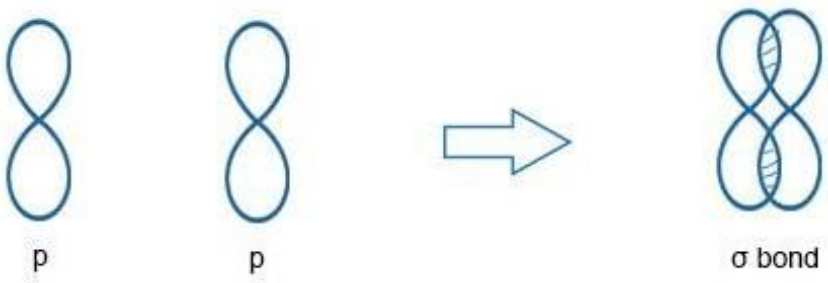




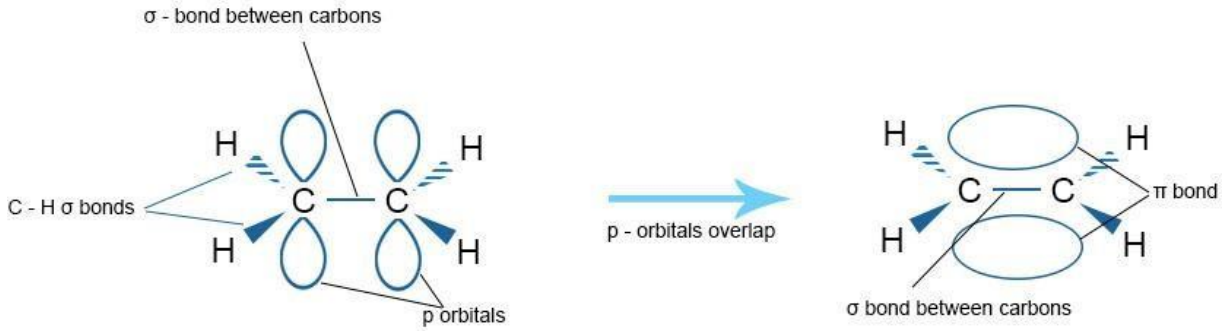


π bond

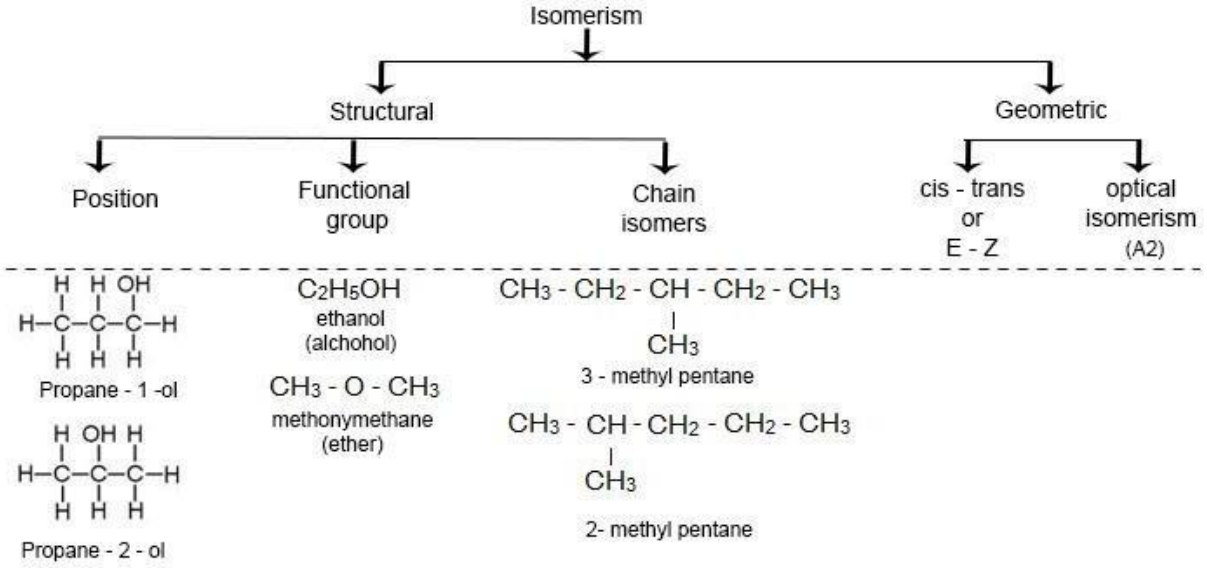
π bond is formed when two p orbitals overlap sideways.



- In sigma bonds the electron cloud is concentrated between the two nuclei.
- In pi bonds the electron cloud is not in a line between the two nuclei, but above and below the plane of the molecule.
- σ bond is stronger than π bond.
- Atoms bonded by a σ bond can rotate about its axis, but the π bond does not allow rotation and thus affects the structure and reactions of alkenes.
- In π bond, the electron density is higher and so alkenes are more accessible to electrophilic attack.
- All single bonds are σ bond.
- The multiple bonds have one sigma bond and others are π bond.



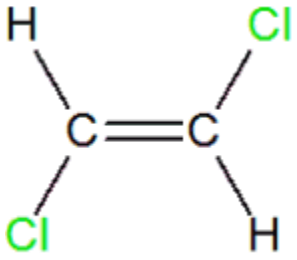
b explain E-Z isomerism (geometric/cis-trans isomerism) in terms of restricted rotation around a C==C double bond and the nature of the substituents on the carbon atoms



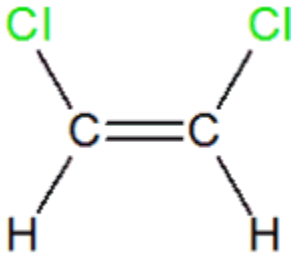
The lack of free rotation around the double bond in but-2-ene results in molecules known as geometric isomers. Geometric isomers occur when components of the molecule are arranged on different sides of the molecule.

cis – trans isomers

The traditional way of naming geometric isomers is known as cis-trans isomerism.



trans-1,2-dichloroethene



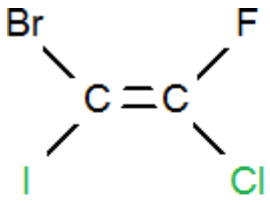
cis-1,2-dichloroethene

trans isomers have the functional groups on the opposite side of the double bond.

cis isomers have the functional group on the same side of the double bond.

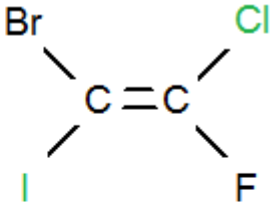
In cis-trans isomerism, the group on either side should be same.

E – Z isomers



Z - isomer

Z - 1 - bromo - 2 - chloro - 2 - fluro - 1 - iodo ethene



E - isomer

E - 1 - bromo - 2 - chloro - 2 - fluro - 1 - iodo ethene

When the highest ranking groups on each carbon are on the same side of the double bond, they are zusammen (together) and this is Z – isomer.

When the highest ranking groups on each carbon are on the opposite side of the double bond, they are entgegen (opposite) and this is E – isomer.

These ranks are based on atomic number – the higher the atomic number, the higher the rank.

Geometric isomers frequently show different physical properties. Their melting and boiling temperatures as well as the density of the compound are often affected. Sometimes the

chemical reaction of the isomers are influenced too, but often the chemical reactivity of the isomers is the same.

c demonstrate an understanding of the E-Z naming system and why it is necessary to use this when the cis- and trans- naming system breaks down

The cis-trans system for naming geometric isomers has been used for many years. However, it has some limitations because the system does not work for all geometric isomers. The IUPAC system for naming geometric isomers is now the system of E-Z isomerism. Although you will still come across cis-trans isomers, the E-Z system is better because it works for all geometric isomers.

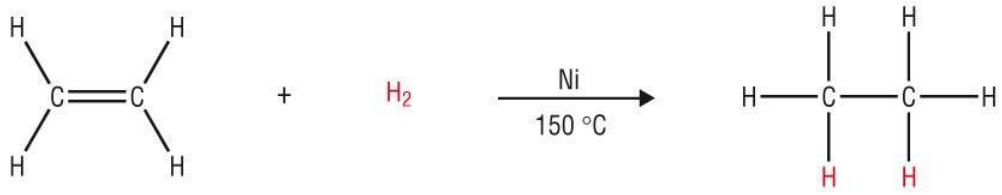
d describe the addition reactions of alkenes, limited to:
i the addition of hydrogen with a nickel catalyst to form an alkane
ii the addition of halogens to produce di-substituted halogenoalkanes
iii the addition of hydrogen halides to produce mono-substituted halogenoalkanes
iv oxidation of the double bond by potassium manganate(VII) to produce a diol

The C = C double bond is alkenes makes them much more reactive than the alkeanes. Alkenes react across the double bond – an addition reaction with another substance to form a single, saturated product. The reactions you have to know are:

- alkene + hydrogen → alkane
- alkene + halogen → halogenoalkane
- alkene + hydrogen halide → halogenoalkane
- alkene + acidified $KMnO_4$ → a diol

i) Addition of hydrogen

This is called catalytic hydrogenation. It is used in the manufacture of margarine to turn unsaturated vegetable oil into a soft, saturated fat. It has to be done at around 200°C in the presence of a finely divided (high surface area) nickel catalyst.



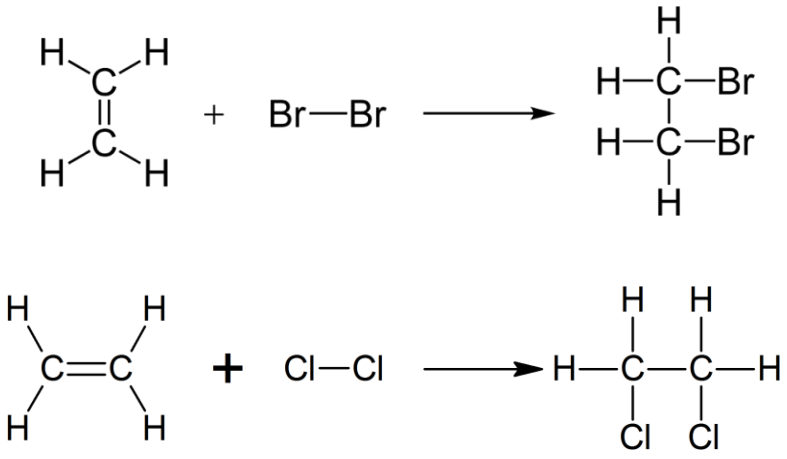
Ethene
unsaturated

Ethane
saturated

ii) Addition of halogens

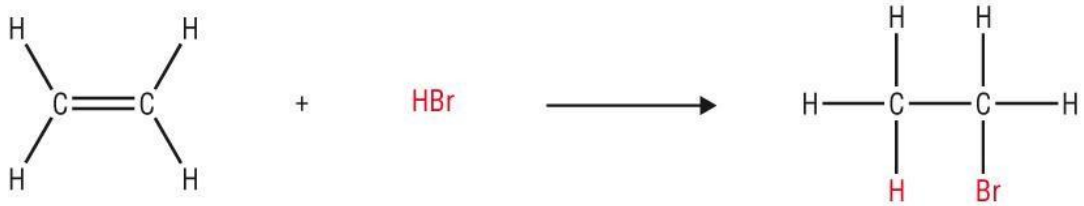
Ethene reacts with bromine or bromine water to produce the halogenoalkane called 1, 2-dibromo ethane, CH_2BrCH_2Br. This is disubstituted halogenoalkane The bromine is decolorized in the reaction and the product is a colourless liquid.

The other halogens also react with alkenes to produce disubstitued halogenoalkanes. This is an addition reaction and the mechanism is described below.



iii) Addition of hydrogen halides

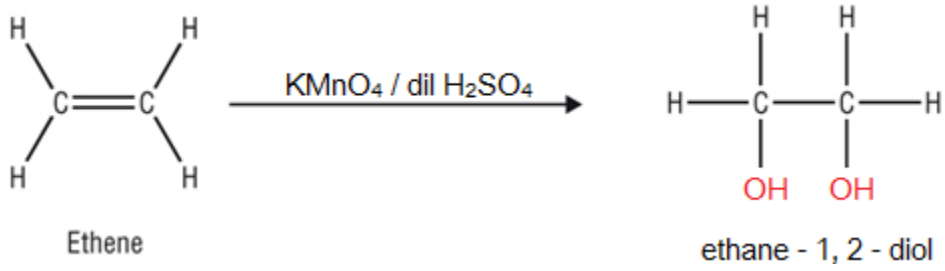
Ethene reacts with hydrogen bromide to produce the halogenoalkane bromoethane, CH_3CH_2Br. This is a monosubstituted halogenoalkane.



Ethene Bromoethane

iv) Reaction with acidified potassium manganate (VII)

Potassium manganate (VII) ($KMnO_4$) is acidified with dilute sulfuric acid. The reaction results in oxidation of the alkene to form a diol (with two –OH groups). The potassium manganite (VII) is decolourised – it changes from purple to colourless. This reaction can also be used as a test for alkenes.



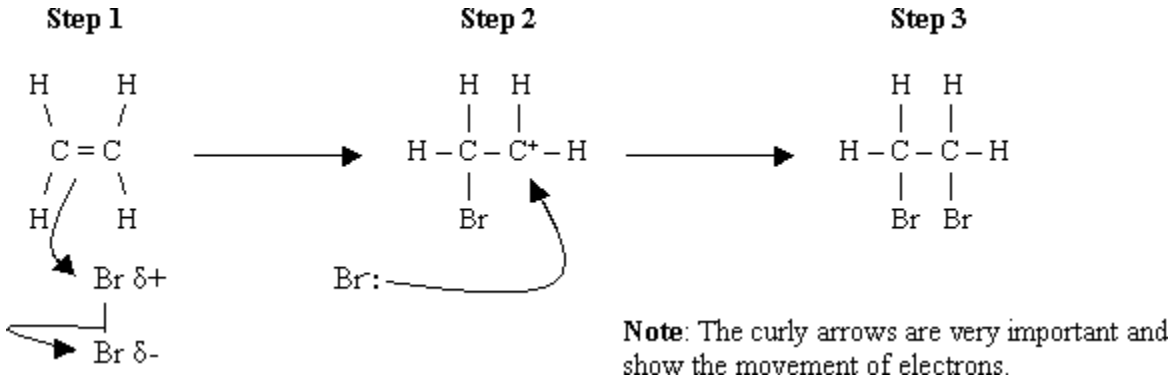
e describe the mechanism (including diagrams), giving evidence where possible, of: i the electrophilic addition of bromine and hydrogen bromide to ethene ii the electrophilic addition of hydrogen bromide to propene

i) Addition of bromine – the mechanism

When bromine approaches the double bond in the ethane, its electron cloud shifts due to the repulsion from the high electron density – this shift produces an instantaneous **dipole** (bromine with positive and negative charge). This polarized bromine acts as an **electrophile** and attracts an electron pair from the double bond to form a covalent C – Br bond, a positive **carbocation** (the ion formed after one of the carbon atoms in ethane molecule gains a positive charge) and a bromide ion – this is **an electrophilic attack**.

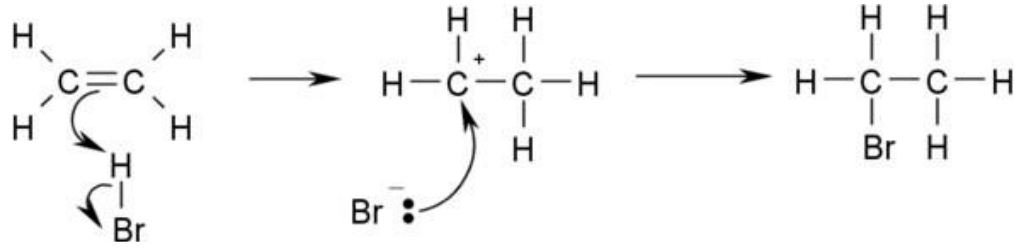
The bromide ion acts as a **nucleophile** now attacks the carbocation – this is a **nucleophilic attack**.

Overall, the mechanism is called **electrophilic addition**.



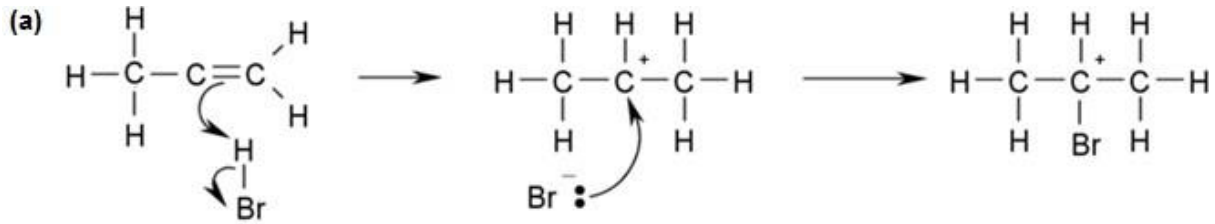
Addition of hydrogen bromide – the mechanism

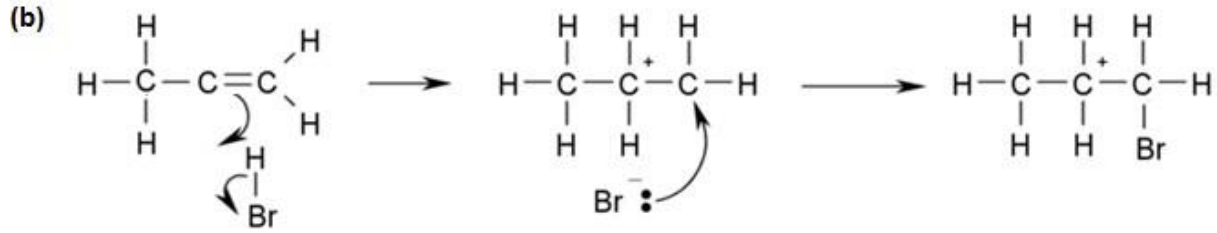
The HBr molecule has a permanent dipole. HBr acts as **electrophile** and attracts an electron pair from the double bond. Therefore, the mechanism is the same as that of bromination of ethane.



ii) Addition of hydrogen bromide to propene

This is also an **electrophilic addition** reaction, but because propene is asymmetrical there are two possible products.

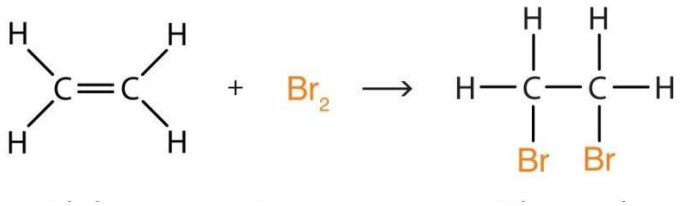




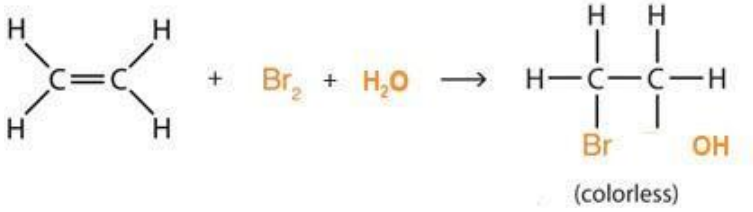
- The secondary carbocation formed in (a) is more stable because the methyl groups on either side donate electron density and stabilize the positive charge.
- Therefore the carbocation formed in (a) is longer lived (more stable), than that in (b)

f describe the test for the presence of C==C using bromine water and understand that the product is the addition of OH and Br

- If a compound contains at least one C = C bond it will decolorize bromine water.
- The reaction is an addition reaction, similar to the addition of bromine to an alkene.
- However, in aqueous bromine, both Br^- from the bromine and OH^- from the water can add to the carbocation.
- Two different reactions can take place.

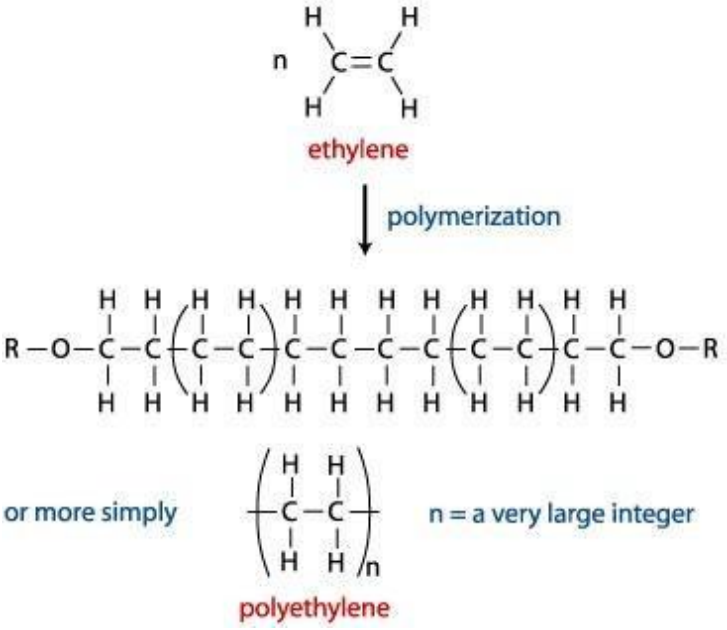


or

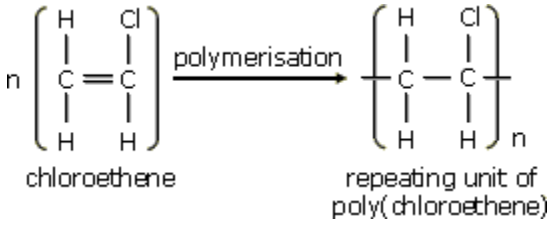


g describe the addition polymerisation of alkenes and identify the repeat unit given the monomer, and vice versa

A **polymer** is formed when a very large number of monomers join together to form a chain. A monomer is a small molecule. Alkenes undergo addition polymerization to form a poly(alkene) – the reaction occurs by addition across the double bond. Polymerisation of ethene uses up all the monomers and form one desired product. Therefore, its atom economy is 100%.



A **repeat unit** is the monomer with the double bond replaced by a single bond and two side links drawn. Many polymer formulae include the letter n to represent the number of monomer molecules linked – in the case of some polymers n will be around 10,000 to 20,000 or bigger!



A monomer alkene can be identified from a polymer – it includes a C = C bond and four groups attached to the two carbon atoms.

h interpret given information about the uses of energy and resources over the life cycle of polymer products to show how the use of renewable resources, recycling and energy recovery can contribute to the more sustainable use of materials.

Polymers are made from chemicals derived from crude oil, therefore they:

- have high-energy production costs
- use up non-renewable resources

Disposal of synthetic polymers is a huge problem as they are non-biodegradable (taking up landfill space long-term) and burn to produce toxic gases.

Using renewable or alternative energy resources in the manufacture of polymers reduces the effect on the environment and conserves fossil fuels.

The benefits of recycling polymers are reduction in the:

- consumption of finite oil resources
- need for disposal of plastic
- carbon footprint (mass of carbon dioxide produced in a process)
- energy consumed in manufacture of the product
- consumption of water during manufacture.

But recycling has its own energy costs:

- transport of the material to processing plants
- energy consumed in sorting, melting or shredding

- transport of the new products.

Energy recovery is a new approach to reducing the energy consumption of polymer manufacture. Energy recovery can generate electricity and produce hot water from the high-temperature **incineration** of plastic waste. The very high temperature ensures that toxic gases, such as dioxins, are not produced. The use of plastic waste reduces the amount of fossil fuel used to generate power and heat.

A **lifecycle analysis** quantifies the energy and materials used and any environmental emissions produced during the extraction of raw materials, original manufacture, recycling, reuse or disposal of polymer product.

Unit 2: Application of Core Principles of Chemistry

Topic: Shapes of Molecules and Ions

a demonstrate an understanding of the use of electron-pair repulsion theory to interpret and predict the shapes of simple molecules and ions

Electron pair repulsion theory is a model that predicts the shape of a covalent molecule around a central atom:

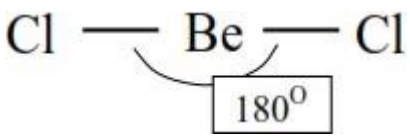
- The shape of the molecule depends on the number of electron pairs, including bonding pairs and non-bonding pairs of electrons.
- These pairs of electrons repel each other because they have the same negative charge. They try to get as far as apart as possible to minimize the repulsion.

Shape of molecules

Linear bond

If there are two bond pair electrons around the central atom, they form linear shaped molecule. The bond angles will be 180°. As said, this is to minimize the repulsion and maximize the separation.

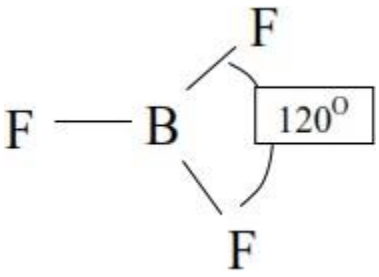
e.g.: Beryllium chloride



Trigonal planar

If three bond pair electrons are there around the central atom, then the shape of the molecule will be trigonal planar. The bond angle is at 120°.

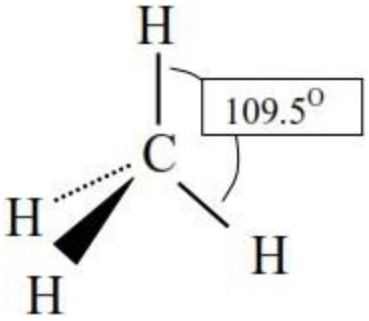
e.g.: Beryllium fluoride



Tetrahedral

If four bond pair electrons are there, then the shape of the molecule will be tetrahedral. The bond angle will be 109.5°.

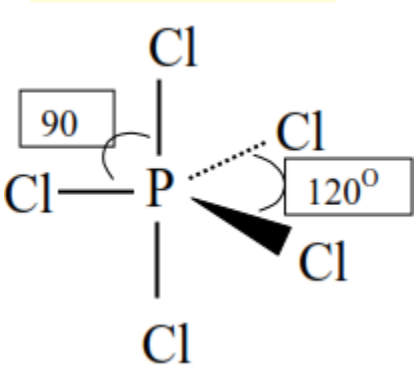
e.g.: Methane



Trigonal bipyramidal

If five bond pair electrons are there, then the shape will be trigonal bipyramidal. The bond angles will be 90° and 120°.

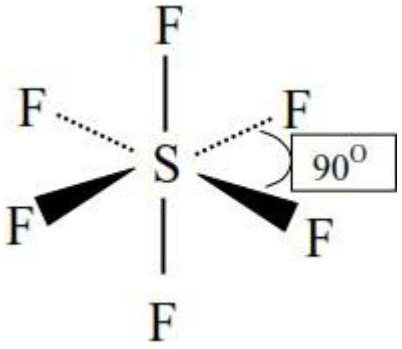
e.g.: Phosphorus pentachloride



Octahedral

If six bond pair electrons are there, then the shape will be octahedral. The bond angles will be 90^o.

e.g.: Sulfur hexafluoride



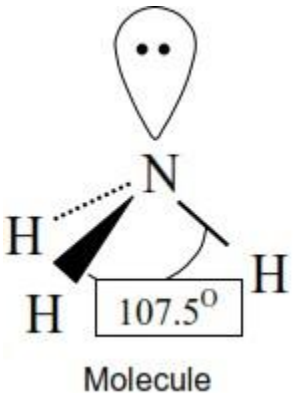
Non-bonding electrons

For the involvement of lone pairs of electrons, apply the following rules:

- Lone pairs repel more than bonding pairs because they are attracted to a single nucleus and not shared by two atoms.
- Lone-pair repulsion reduces the bond angle between bonding pairs. Each lone pair of electrons reduces the predicted bond angle between bonding electrons by 2.5^o.

e.g.:

$\underline{NH_3}$

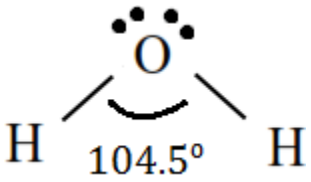


Molecule

Ammonia has three bonding electron pairs and a lone pair of electrons in the valence shell. These position themselves as far apart as possible, but the lone pair has a greater repulsion

than the bonding pairs pushing the bonding pairs closer together and reducing the bond angle to 107.5° (109.5 – 2.5). The molecule is pyramidal.

H_2O



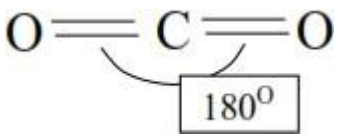
Water has two bonding electron pairs and two lone pairs of electrons in the valence shell. The two lone pairs have a greater repulsion than the bonding pairs, pushing the bonding pairs closer together and reducing the bond angle to 104.5° (109.5 – 2 x 2.5). The molecule's shape is bent-linear.

Multiple bonds

Ignore the presence of multiple bonds, just count it as one pair.

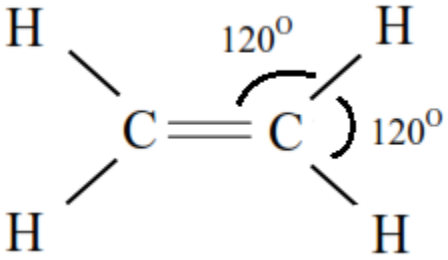
e.g.:

CO_2



Carbon dioxide molecule has two double bonds and so forms a linear molecule.

C_2H_4



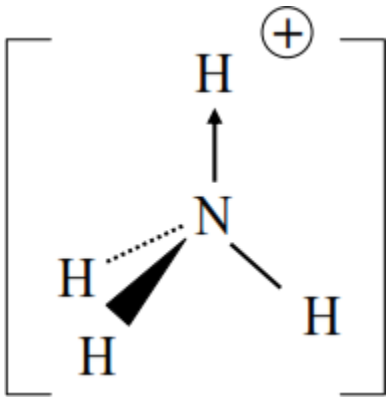
In the ethane molecule, each carbon atom has one double bond and two single bonds – the resulting shape is trigonal planar.

Shape of ions

The charge here is ignored, shape is predicted in the same way. Except, a positive and a negative charge means that there is an extra electron and a short of electron respectively.

e.g.:

$\underline{NH_4^+}$

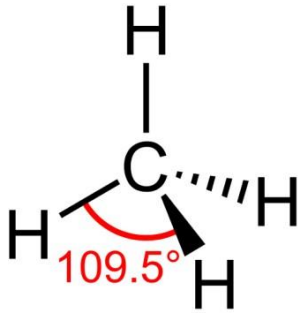


The ammonium ions has four bonding pairs of electrons in the valence shell (one of these being a dative bond). The molecule is tetrahedral with bond angles of 109.5°.

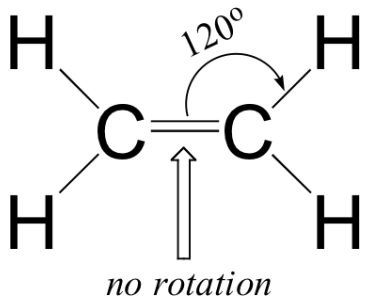
b recall and explain the shapes of $BeCl_2$, BCl_3, CH_4, NH_3, NH_4^+, gaseous PCl_5 and SF_6, H_2O, CO_2 and the simple organic molecules listed in Units 1 and 2

Follow (a)

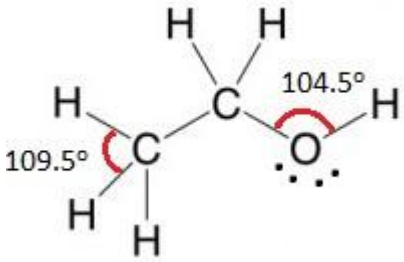
1. Alkane



2. Alkene



3. Ethanol



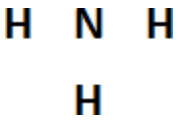
c apply the electron-pair repulsion theory to predict the shapes of molecules and ions analogous to those in 2.3b

Summary: How to find the shape of any molecule?

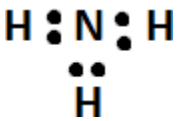
The following example will be carried out for NH_3

Steps:

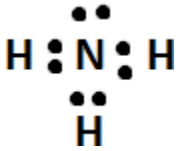
1. Find valence electrons:
   1 N = 5 x 5 e^- = 5 e^-
   3 H = 3 x 1 e^- = 3 e^-
   = 8 e^- (in total)
2. Draw the molecule so that the singular atom is in the middle.



3. Draw the bonds.

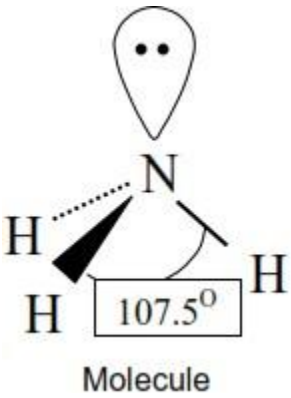


4. Draw the lone pairs if any.



In this case, after adding the bonds, 2 electrons was remaining from the valence electrons. So we have one lone pair of electrons.

5. Name its shape by judging the number of bonds and lone pairs. In this case it is trigonal pyramidal because of 3 bonds and 1 lone pair. However, lone pair repels more and decreases the other bond angles by 2.5.



Molecule

d demonstrate an understanding of the terms bond length and bond angle and predict approximate bond angles in simple molecules and ions

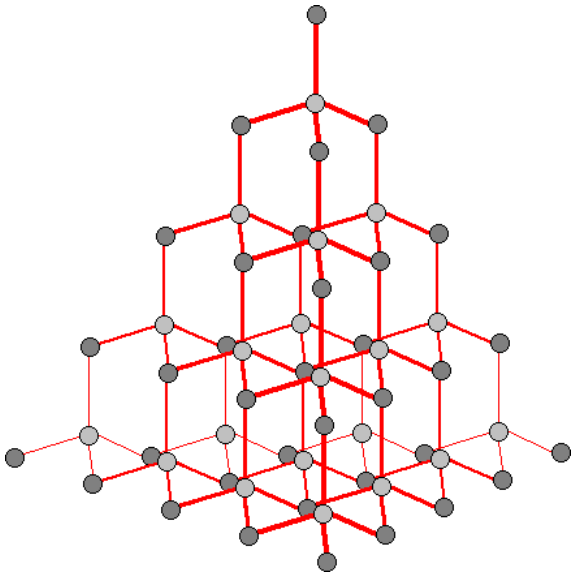
The distance between the two nuclei in a covalent bond is called bond length. The bond length in a double bond is smaller than a single bond. A triple bond is smaller than a double bond.

e.g.: The distance between hydrogen nuclei in a hydrogen molecule is 0.074 nm.

e discuss the different structures formed by carbon atoms, including graphite, diamond, fullerenes and carbon nanotubes, and the applications of these, e.g. the potential to use nanotubes as vehicles to carry drugs into cells.

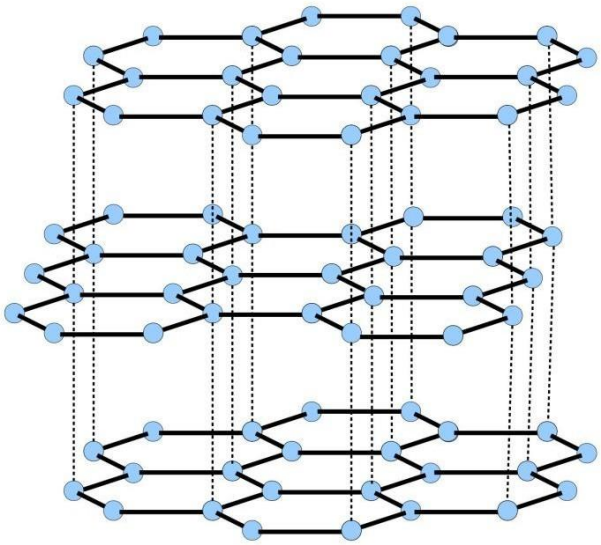
Diamond: Diamond is composed of carbon atoms. Each carbon atom is connected to four other carbon atoms. Each of these atoms is also connected to three other carbon atoms. In this way a giant structure is built up from these tetrahedral units. This structure, held together by strong covalent bonds, is very difficult to break apart. So diamond has very high melting and boiling points. It is the hardest natural substance. Since all the electrons are taken up in bonding, diamond is a non-conductor.

Diamond are attractive which means they are used as jewellery. Its hardness makes it useful for cutting instruments such as drill tips.

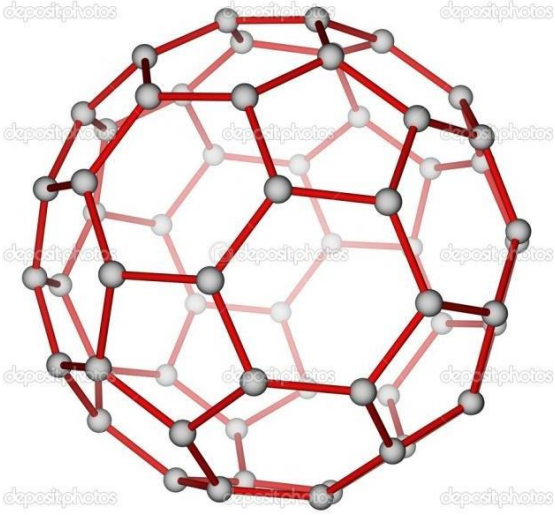


Graphite: Graphite consists of carbon atoms in layers. Within a layer, each carbon is strongly bonded to three other carbon atoms at 120^{o}, so the melting and boiling points are high. The layers are only weakly bonded to each other which makes the layers slide over each other, making a soft slippery substances. The fourth outer electron from carbon is delocalized and free to move, so graphite is a good conductor.

Graphite can be used for electrodes as it is a conductor, and unlike metals it does not react during electrolysis. It can be used as a lubricant because of its slippery nature.



Fullerene: A football shaped molecule which is another allotrope of carbon. In this allotrope, 60 carbon atoms are linked to form a spherical molecule. The full name is buckminister fullerene which is a black solid that dissolves in petrol to form a deep-rod solution. Like graphite, it has electrons that are free to move. So it can conduct electricity.



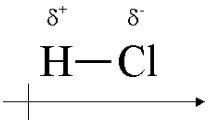
Nanotubes: A nanotube can be regarded as grapheme which has rolled up to form a cylinder. Grapheme is the single layer in graphite. Nanotubes are good conductors of electricity. It can be used as vehicles to carry drugs into cells.

Intermediate Bonding and Bond Polarity

a explain the meaning of the term electronegativity as applied to atoms in a covalent bond

The electronegativity of an element measures the ability of an atom to attract an electron pair to itself in a covalent bond.

e.g.



- Electronegativity increases across a period from left to right.
- Electronegativity decreases down the group.
- The highest electronegativity is 4.0 (fluorine).
- The range for the electronegativity is from 0 to 4.
- Caesium has the least electronegativity.

The table below shows electronegativity values of main block elements

		H 2.1						He
Li 1.0	Be 1.5		B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne
Na 0.9	Mg 1.2		Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar
K 0.8	Ca 1.0		Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr
Rb 0.8	Sr 1.0		In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe
Cs 0.8	Ba 0.9		Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2	Rn

b recall that ionic and covalent bonding are the extremes of a continuum of bonding type and explain this in terms of electronegativity differences leading to bond polarity in bonds and molecules, and to ionic bonding if the electronegativity is large enough

The difference in electronegativity in a covalent bond creates polarity in the molecule. e.g. In HCl, chlorine is more electronegative than hydrogen. So the hydrogen chloride molecule is

polar. There is a degree of covalency in ionic compound and it can be measured by measuring the difference of electronegativity between them.

Calculate the percentage of ions and covalent boning in

a) lithium fluoride

electronegativity of lithium = 1.0
electronegativity of fluorine = 4.0
the difference = 3.0

Therefore, lithium is 89% ionic and 11% covalent.

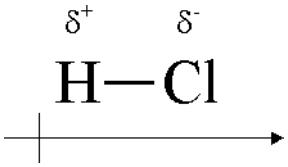
b) ammonia

electronegativity of nitrogen = 3.0
electronegativity of hydrogen = 2.1
the difference = 0.9

Therefore, ammonia is 19% ionic and 81% covalent.

c distinguish between polar bonds and polar molecules and be able to predict whether or not a given molecule is likely to be polar

Polar bond: If there is a difference in electronegativity between two atoms in a molecule (above 0.7 and below 1.7), then the bond is said to be polar. e.g.



Polar molecule: If the molecule has symmetrically charge distribution, then the molecule is said to be non-polar, though the bonds maybe polar. e.g.: carbon dioxide. Shapes that are symmetrical are: linear, trigonal planar, tetrahedral, trigonal bipyramidal, octahedral, square planar. In these shapes, if the atoms attached to the central atom are identical, the dipoles will cancel out and it will be a non-polar molecule.

And, if a molecule has asymmetrical charge distribution, then the molecule become polar. e.g. carbon monoxide, ammonia etc.

How to determine the molecule is polar or not?

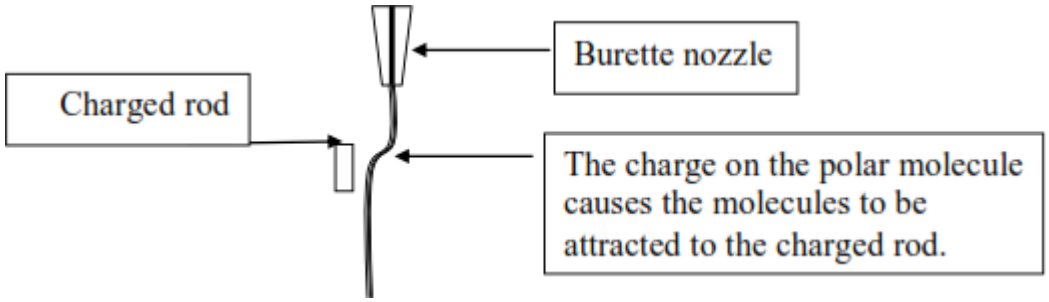
Follow these steps in order to find it:

1. Draw the molecule's shape.
2. Determine if the bonds are polar.
3. Determine its shape.
   a. If the dipoles are asymmetrical then it is polar.
   b. If the dipoles are symmetrical then it is nonpolar.

d carry out experiments to determine the effect of an electrostatic force on jets of liquids and use the results to determine whether the molecules are polar or non-polar.

Experiment: To determine whether the molecules are polar or non-polar.

A fine jet of polar molecule will be attracted towards an electrically charged plastic rod or comb.



The molecules are always attracted to charged rod, whether it is positively charged or negatively charged. This is because molecules have both positively and negatively charged ends. The forces between two molecules having permanent dipole-dipole force.

Topic 7: Intermolecular Forces

a demonstrate an understanding of the nature of intermolecular forces resulting from interactions between permanent dipoles, instantaneous dipoles and induced dipoles (London forces) and from the formation of hydrogen bonds

Nature of intermolecular force:

i. Van der Wall force/ London force/ Instantaneous dipoles and induced dipoles
ii. Permanent dipole-dipole force
iii. Hydrogen bond

Van der Wall: It occurs in between non-polar molecule.

Procedure: The electron clouds in a non-polar molecular are constantly moving. At an instant, for a short moment the electron cloud is on one side of the molecule than the other. So it has more negative charge on side than the other – a temporary induced charge is set up. These dipole can set up a dipole on neighbouring molecule. As a result there is positive attraction at an end of one molecule and the negative end on the dipole on neighbouring molecule.

Factors that increases van der Wall force:

i. Increasing number of electrons in the molecule.
ii. Increasing the number of contact point between the molecules.

Permanent dipole-dipole: It occurs in between two polar molecules (the positive poles attract the negative poles). This attraction force is stronger than the van der Wall force. This force increases when the difference in electronegativity between atoms increases.

Hydrogen bond: Hydrogen bond are special type of permanent dipole-dipole force. For hydrogen bonds to form, there must be: a hydrogen atom bonded directly to a highly electronegative atom. e.g.: nitrogen, oxygen or fluorine.

If a molecule contains H – N, H – F, H – O bonds, they will form hydrogen bond. e.g. water, fluoride, ammonia.

Hydrogen bonds are stronger than permanent dipole – dipole force.

b relate the physical properties of materials to the types of intermolecular force present, e.g.:

i the trends in boiling and melting temperatures of alkanes with increasing chain length

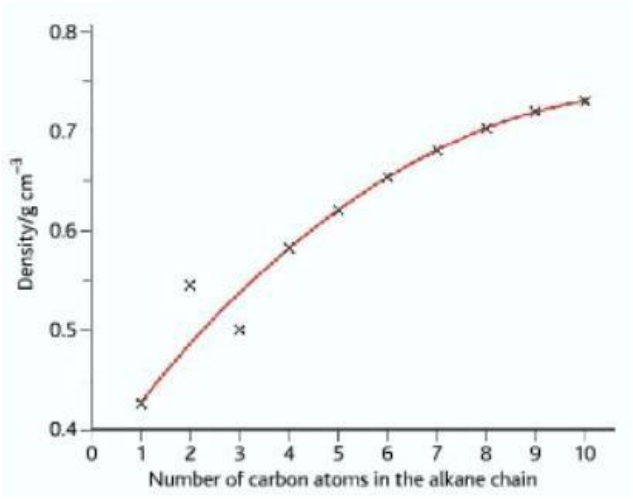
ii the effect of branching in the carbon chain on the boiling and melting temperatures of alkanes

iii the relatively low volatility (higher boiling temperatures) of alcohols compared to alkanes with a similar number of electrons

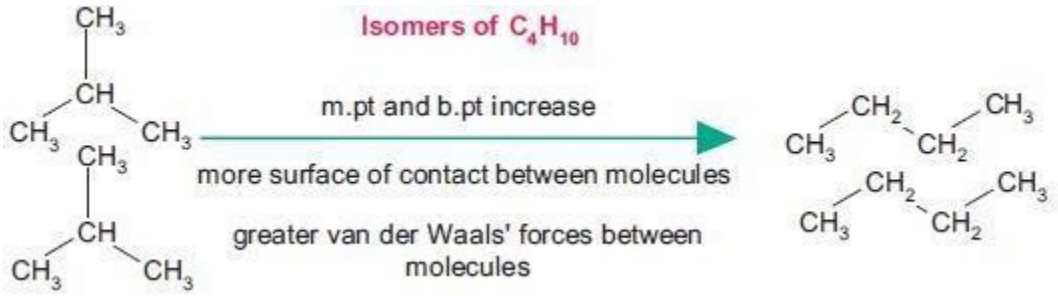
iv the trends in boiling temperatures of the hydrogen halides HF to HI

The boiling temperatures of liquids are determined by intermolecular forces. The stronger thte intermolecular forces, the higher the boiling temperature.

i) The boiling temperature of alkanes increases as the chain length increases. This is because the intermolecular London forces are stronger for larger molecules.

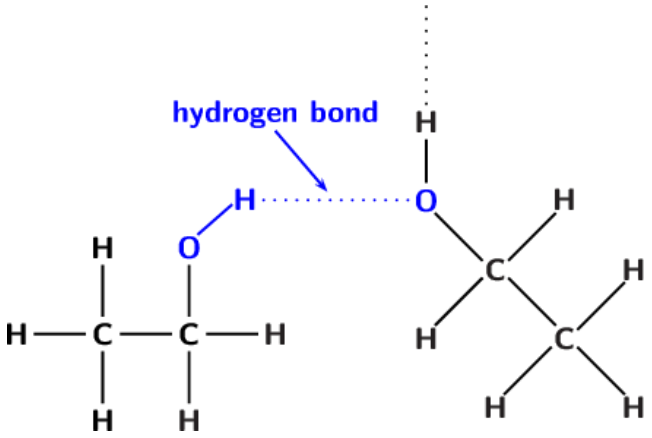


ii) London forces are stronger between straight-chain alkane molecules than between branched alkane molecules with the same number of carbon atoms. This is because the chains can line up with each other (greater surface area in contact) to maximize the force. This is the reason why 2-methylpropane has a lower boiling temperature than its isomer butane.

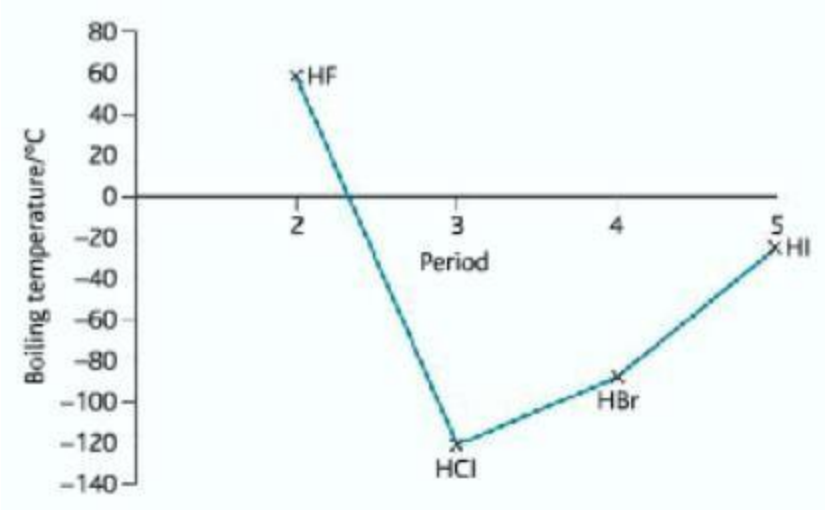

Isomers of C4H10
m.pt and b.pt increase
more surface of contact between molecules
greater van der Waals' forces between molecules

iii) Hydrogen bonding explains why alcohols have much higher boiling temperatures (lower volatility) than alkanes of similar molar mass and a similar number of electrons. For example,

ethanol, M_r = 46, boils at 79°C while butane, M_r = 44, boils at -42°C. Both have similar London forces because they have similar number of electrons. But ethanol can form additional hydrogen bonds between molecules.



iv) The boiling temperature of hydrogen halides rises from HCl to HI because the London forces are stronger due to increasing number of electrons. Hydrogen fluoride is exceptional – it has weaker London forces because it has the fewest electrons. However, it has much higher boiling temperature than the other hydrogen halides. The reason is that it has additional hydrogen bonds.



c carry out experiments to study the solubility of simple molecules in different solvents

Rule:

- If the forces of attraction between the molecules of one liquid are stronger than the intermolecular forces between the molecules of the two different liquids, then the liquids do not mix. Because the energy given out when new attractions form between

the two liquids will be insufficient to overcome the energy required to break the existing forces.

- Polar liquids dissolve only in polar liquids but not in non-polar liquids. Non-polar liquids only dissolve in non-polar liquids, not in polar liquids.

d interpret given information about solvents and solubility to explain the choice of solvents in given contexts, discussing the factors that determine the solubility including:

i the solubility of ionic compounds in water in terms of the hydration of the ions

ii the water solubility of simple alcohols in terms of hydrogen bonding

iii the insolubility of compounds that cannot form hydrogen bonds with water molecules, e.g. polar molecules such as halogenoalkanes

iv the solubility in non-aqueous solvents of compounds which have similar intermolecular forces to those in the solvent.

i) The water molecules are polarized. So that hydrogen atoms are positive charged and oxygen atoms have negative charge. Attractive forces between the water molecules and the ions in the lattice break up. The lattice and the individual ions begun spread throughout the water.

The process of water molecules arranging themselves around an ion is called hydration and the energy released when this happens is called hydration enthalpy.

ii) Alcohols are soluble in water because they have polar O – H group that can form hydrogen bond to the OH group in the water molecules.

iii) In non-polar substances, there is much weaker attraction between the molecules than the hydrogen bonds between the water molecules. The non-polar molecules are unable to break the water structure. So, non-polar molecules remain as a separate layer.

iv) When two non-polar liquids are mixed, the weak van der Walls force extends throughout the mixture and mix readily.

Topic 8: Redox Chemistry and Groups 1, 2 and 7

a demonstrate an understanding of:

i oxidation number — the rules for assigning oxidation numbers

ii oxidation and reduction as electron transfer

iii oxidation and reduction in terms of oxidation number changes

iv how oxidation number is a useful concept in terms of the classification of reactions as redox and as disproportionation

i) The applied valence condition of an element in a compound is called oxidation number.

e.g.: The valency of carbon in carbon monoxide is 2. Therefore, the oxidation number here +2.

The valency of carbon in carbon dioxide is 4. Therefore, the oxidation number here is + 4.

The rules for assigning oxidation number

1. Uncombined element have 0 oxidation number.
   e.g.: Fe + $CuSO_4$, here oxidation number of Fe is 0.
2. For monoatomic ions, the oxidation number is equal to the charge:
   e.g.: Fe^{2+}, here oxidation number is +2.
3. For a neutral compound, the total oxidation number is 0.
   e.g.: $H_2SO_4 = 0$
   → +1 x 2 + S + 4(-2) = 0
   → S = +6

   $KMnO_4 = 0$
   → +1 + Mn + 4(-2) = 0
   → Mn = +7
4. For polyatomic ions, the sum of the oxidation number is equal to the charge of the ion.
   e.g.: SO_4^{2-}
   → SO_4 = -2
   → S + 4(-2) = -2
   → S = +6

   Some exception:
   - In metal hydride, the oxidation number of H is – 1. e.g. NaH
   - If oxygen combine with fluorine, the oxidation number of oxygen is +2.

- In hydrogen peroxide, the oxidation number of oxygen is -1.

ii) Oxidation and reduction as electron transfer.

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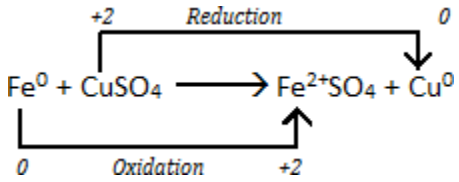
Oxidation is loss of electrons.

Reduction is gain of electrons.

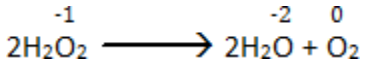
iii) Oxidation is increase in oxidation number (state).

Reduction is decrease in oxidation state. e.g.:



iv) Redox: The reaction in which both oxidation and reduction takes place is called redox reaction.

Disproportionation: A reaction in which one of the reactants is both oxidized and reduced is called disproportionation. e.g.:



The oxygen is reduced and also oxidized in this reaction. So this reaction is disproportionation.

b write ionic half-equations and use them to construct full ionic equations.

$Fe - 2e \rightarrow Fe^{2+}$ (Half eq^n for oxidation)

$Cu^{2+} + 2e \rightarrow Cu$ (Half eq^n for reduction)

$Fe + Cu^{2+} \rightarrow Fe^{2+} + Cu$

Properties down Group II

a explain the trend in the first ionisation energy down group 2

The trend of first ionization energy down group II decreases. Because, atomic radius is increasing as the additional electrons fill higher energy levels. So, the distance between the positive nucleus and the negative electrons is increasing and the force of attraction is less. The shielding of nucleus is also increasing. Inner shell electrons shield the two outer electrons from the nucleus, further reducing the force of attraction. That's why first ionization energy decreases.

b recall the reaction of the elements in group 2 with oxygen, chlorine and water

• All group 2 metals burn in air or oxygen to form solid metal oxides, often burning with a very bright flame. Reactivity increases down the group. e.g.:

$$Mg(s) + ½\ O_2(g) \rightarrow MgO(s)$$

• All the Group 2 metals burn in chlorine to form solid metal chlorides. In general, reactivity increases down the group.

$$Mg(s) + Cl_2 \rightarrow MgCl_2(s)$$

• Calcium and the elements of the group below it react with water similarly to form hydrogen and the corresponding hydroxide. e.g.:

$$Mg(s) + 2H_2O(l) \rightarrow Mg(OH)_2\ (aq) + H_2(g)$$

Beryllium does not react with water, due to the formation of insoluble oxide layer. Magnesium reacts very slowly with cold water, but with steam it reacts vigorously to give magnesium oxide, which is almost insoluble.

$$Mg(s) + H_2O(g) \rightarrow MgO\ (aq) + H_2(g)$$

c recall the reactions of the oxides of group 2 elements with water and dilute acid, and their hydroxides with dilute acid

• From calcium down the group, the oxides react with water to form the corresponding hydroxides. e.g.:

$$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(aq)$$

Calcium hydroxide has many uses in water purification, and making whitewash, mortar and plaster.

• All the oxides neutralize hydrochloric acid and nitric acid to form the corresponding chlorides or nitrates:

$$MgO(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2O(l)$$

$$CaO + 2HNO_3(aq) \rightarrow Ca(NO_3)_2(aq) + H_2O(l)$$

• The hydroxides of the Group 2 elements react with dilute acids in a similar way:

$$Sr(OH)_2(aq) + 2HCl(aq) \rightarrow SrCl_2(aq) + 2H_2O(l)$$

d recall the trends in solubility of the hydroxides and sulfates of group 2 elements

- The solubility of hydroxides increases down the group. Calcium hydroxide is slightly soluble giving a solution called limewater. The solution reacts with carbon dioxide to form a white precipitate of calcium carbonate, $CaCO_3$. On further addition of carbon dioxide, the solution clears because soluble calcium hydrogencarbonate forms, $Ca(HCO_3)_2$.
- The solubility of sulfates decreases down the group. Again, calcium sulfate is somewhere in between soluble and insoluble. Barium sulfate is used in 'barium meal' X-ray investigations because it is insoluble, and so it is not absorbed from the gut. It is useful to use barium compounds, despite their poisonous nature, because barium shows up well on X-rays because it has so many electrons.

e recall the trends in thermal stability of the nitrates and the carbonates of the elements in groups 1 and 2 and explain these in terms of size and charge of the cations involved

Thermal stability means the stability of a compound when it is heated. The carbonates and nitrates of Groups 1 and 2 follow the same patterns of thermal stability.

- From sodium carbonate down Group 1, the carbonates do not decompose on heating.
- From sodium nitrate down Group 1, the nitrates decompose to form the corresponding nitrite and oxygen. e.g.:
  $KNO_3(s) \rightarrow KNO_2(s) + ½\ O_2(g)$
- Lithium carbonate, and all the Group 2 carbonates, decompose on heating to form carbon dioxide and the corresponding oxide. e.g.:
  $Li_2CO_3(s) \rightarrow Li_2O(s) + CO_2(g)$
  $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

- Lithium nitrate, and all Group 2 nitrates, decompose on heating to form oxygen, nitrogen dioxide and the corresponding oxide.
  $4LiNO_3 \rightarrow 2Li_2O + 4NO_2 + O_2$

Going down Group 2, both the carbonates and nitrates become more stable to heat. This is because the ionic radius of the positive ion increases down the group and the oxides with smaller ions are more stable, due to the polarization of the oxide ions giving additional covalent bonding.

f recall the characteristic flame colours formed by group 1 and 2 compounds and explain their origin in terms of electron transitions

Nichrome wire is used because it is unreactive. Concentrated hydrochloric acid is used because chlorides are soluble and volatile.

Procedure:

i. Mix the acid and powdered salt and pick up a small sample on the wire.
ii. Hold the coated wire in a roaring Bunsen flame.
iii. The colours produced are:
    - sodium – yellow flame
    - potassium and caesium – lilac flame
    - lithium, strontium – red flame
    - calcium – brick red
    - barium – green flame
    - magnesium – colourless flame

The colours arise because – electrons are given energy and excited to higher energy levels. As they fall back to lower energy levels, energy is relased in the form of visible light (except in the case of magnesium when the radiation given out is outside the visible region of the electromagnetic spectrum).

g describe and carry out the following:

i experiments to study the thermal decomposition of group 1 and 2 nitrates and carbonates

ii flame tests on compounds of group 1 and 2

iii simple acid-base titrations using a range of indicators, acids and alkalis, to calculate solution concentrations in g dm^{-3} and mol dm^{-3}, e.g. measuring the residual alkali present after skinning fruit with potassium hydroxide

i) Thermal decomposition of magnesium nitrate 6-water:

$$Mg(NO_3)_2.6H_2O(s) \rightarrow MgO(s) + ½\ O_2(g) + 2NO_2(g) + 6H_2O(l)$$

When carried out in laboratory, you would expect to see:

- the solid dissolving in the water of crystallization
- the solution boiling, and water condensing at the top of the test tube
- a solid reforming as the water boils away
- the solid melting
- and finally a brown gas (nitrogen dioxide) given off, and also a gas that relights a glowing splint.

ii) Follow f

iii) An acid-base titration is a technique that involves using accurate volume measurements to find the concentration of acid or alkali solutions.

- The acid, usually hydrochloric acid, of known concentration, goes in the burette.
- The alkali goes in a conical flask – use a pipette and pipette filler to take a known volume.
- Always use methyl orange indicator, unless you are titrating a weak acid. Methyl orange from yellow in alkali to red in acid – at the end-point it is orange.
- For a weak acid, such as ethanoic acid, use phenolphthalein. This is pink in alkali and colourless in acid – it is very pale pink at the end-point.

Calculating concentrations of unknown solutions

$$n = \frac{V \times\ c}{1000}$$

Where, n is number of moles, V is volume in cm^3 and c is the concentration in mol dm^{-3}.

h demonstrate an understanding of how to minimise the sources of measurement uncertainty in volumetric analysis and estimate the overall uncertainty in the calculated result.

Results of titration – accuracy, precision and reliability

Results of titration experiments should be recorded in a table like this.

	Titration number		
	1	**2**	**3**
Final burette reading /cm^3			
Initial burette reading /cm^3			

Titre /cm^3			

- The first titre is likely to be inaccurate – a rough titration to get an idea where the end point is – so the result is usually discarded.
- It is usual to record reading to the nearest 0.05 cm^3 – this is the limit of **precision** of the burette (the number of significant figures or decimal places that can be read).
- To improve **reliability**, the experiment should be repeated until you have two **concordant** titres, within 0.20 cm^3. Then the mean of these two should be found.

When you are carrying out titrations you need to eliminate **systematic errors** as far as possible. Some of these are errors caused by poor technique. You must read the burette at eye level – this means it is unlikely that your first burette reading will be 0.00 cm^3. You should also check the burette jet is filled and remove the funnel used to fill your burette.

Measurements uncertainties are caused by random errors, caused by the limits of accuracy of your apparatus. Repeating an experiment will make the results more reliable, but the uncertainties will remain the same if the same apparatus is used.

Estimating uncertainties in your final answer

$$percentage\ uncertainty = \frac{uncertainty\ in\ the\ value}{value} \times 100\%$$

Inorganic chemistry of group 7 (limited to chlorine, bromine and iodine)

a recall the characteristic physical properties of the elements limited to the appearance of solutions of the elements in water and hydrocarbon solvents

Chlorine is a pale yellow-green gas, which dissolves in water to give a pale yellow-green solution, and dissolves in a hydrocarbon solvent to give a pale yellow-green solution too.

Bromine is a red-brown liquid that is very volatile giving a red-brown gas. It is partially soluble in water and very soluble in a hydrocarbon solvent to give a red-brown solutions in both situations.

Iodine is a grey-black solid, which sublimes on heating to give a purple gas. It is slightly soluble in water giving a pale yellow solution. It is very soluble in a hydrocarbon solvent, giving a pink or red solution. It is soluble in potassium iodide solution to give yellow to brown solution depending on concentration.

The physical state of the halogens at room temperature reflect the strength of the intermolecular forces. As the number of electrons increase, the London forces increase in strength. Iodine, with 106 electrons, is a solid while chlorine, with 34 electrons, is a gas.

The halogens are more soluble in a hydrocarbon solvent than in water, because there are more strong London forces between the solvent and the halogens. The halogens cannot form hydrogen bonds with water so are slightly soluble.

b describe and carry out the following chemical reactions of halogens:

i oxidation reactions with metal and non-metallic elements and ions such as iron(II) and iron(III) ions in solution

ii disproportionation reactions with cold and hot alkali, e.g. hot potassium hydroxide with iodine to produce potassium iodate(V)

(i) Halogens are powerful oxidizing agents. It gains one electron and form halide ions. That's why halogens can be used as oxidizing agents.

<u>Oxidation reaction with metals</u>

$2Na + Cl_2 \rightarrow 2NaCl$

$Fe + Cl_2 \rightarrow FeCl_3$

<u>Oxidation reaction with non-metals</u>

$H_2 + Cl_2 \rightarrow 2HCl$

$P + Cl_2 \rightarrow PCl_5$

Oxidizing ions such as iron(II) and iron (III)

Chlorine oxidizes iron(II) to iron (III), causing a pale green solution to turn brown.

$Fe^{2+} + ½\ Cl_2 \rightarrow Fe^{3+} + Cl^-$

Oxidizing power decreases down the group. And elements in the upper position of the group can oxidize the halides of the lower position. e.g.:

$Cl_2 + 2I^- \rightarrow 2Cl^- + I_2$

$Br_2 + 2I \rightarrow 2Br^- + I_2$

(ii) Disproportionation is a specific type of redox reaction in which an element is simultaneously reduced and oxidised to form two different products.

With cold alkali

At 15°C chlorine react with dilute sodium hydroxide and produces sodium chloride and sodium chlorate (I).

$NaOH\ (aq) + Cl_2\ (aq) \rightarrow NaCl\ (aq) + NaOCl\ (aq) + H_2O\ (l)$
$\qquad\qquad\qquad 0 \qquad\qquad -1 \qquad\qquad +1$

With hot alkali

If chlorine is passed into hot concentrated solution of sodium hydroxide, the disproportionation goes further, forming chlorate (V) and chloride.

$6NaOH\ (aq) + 3Cl_2\ (aq) \rightarrow NaClO_3\ (aq) + 5NaCl\ (aq) + 3H_2O\ (l)$
$\qquad\qquad\qquad 0 \qquad\qquad +5 \qquad\qquad -1$

Similar reactions occur for bromine and iodine.

c carry out an iodine/thiosulfate titration, including calculation of the results and evaluation of the procedures involved, e.g. determination of the purity of potassium iodate(V) by liberation of iodine and titration with standard sodium thiosulfate solution

Titration can be used to find the concentration of an iodine solution. It is titrated with sodium thiosulfate solution of known concentration.

The reaction between iodine and thiosulfate ions

The reaction between iodine and thiosulfate is a redox reaction. Iodine is reduced to iodide ions and thiosulfate is oxidized:

I_2 (aq) + $2e^-$ → $2I^-$ (aq) reduction

$2S_2O_3^{2-}$ (aq) → $S_4O_6^{2-}$ (aq) + $2e^-$ oxidation

Adding these gives the full ionic equation:

I_2 (aq) + $2S_2O_3^{2-}$ (aq) → $2I^-$ (aq) + $S_4O_6^{2-}$ (aq)

This reaction can be used to work out the concentration of any oxidizing agent that will react with iodide ions to form iodine … including potassium iodate(V).

A known volume of the oxidizing agent, potassium iodate(V), is reacted with iodide ions in excess potassium iodide solution to liberate iodine. The potassium iodide is in excess potassium iodide solution to liberate iodine. The potassium iodide is in excess so that all of the iodate(V) reacts:

IO_3^- (aq) + $5I^-$ (aq) → $3I_2$ (aq) + $3H_2O$ (l)

The iodine that is formed is then titrated with sodium thiosulfate. The colour change in the titration is yellow to colourless. The accuracy of the end point can be enhanced by adding **starch** as an indicator just before the end-point. The blue-black colour disappears at the end-point, showing that all the iodine has just been reacted.

The preparation of potassium iodate(V)

You should know how to prepare potassium iodate (V):

For example, calculate that the amount of iodine needed to react with 10 cm^3 of 4 mol dm^{-3} potassium hydroxide solution is 5.12 g.

Iodine is added until the colour is just visible.

Further drops of potassium hydroxide solution are added until the brown colour turns very pale yellow.

Crystals are formed by precipitation from a hot solution. On cooling, potassium iodate (V) crystallizes before potassium iodide because it is much less soluble in cold water. However, the sample is impure.

The potassium iodate (V) is collected by suction filtration and dried between filter papers.

Finding the purity of a sample of potassium iodate (V)

You need to remember the details of how to make up a standard solution of a known mass (about 0.5g) of impure potassium iodate(V):

- Weigh a weighing bottle with lid.
- Weigh the weighing bottle containing about 0.5g of your sample of potassium iodate (V).
- Tip the contents of your weighing bottle through a funnel into a volumetric flask.
- Rinse your weighing bottle with water, and pour the rinsings through the funnel into the flask.
- Make up the flask to the 100 cm^3 of graduation mark.
- Shake the flask thoroughly.
- Pipette 10 cm^3 of this solution into a 100 cm^3 conical flask.
- Titrate the iodine formed with 0.010 mol dm^{-3} sodium thiosulfate solution.
- Calculate the concentration of the iodine solution, and hence the percentage purity of your sample of potassium iodate(V).

Titration calculation

The steps in this calculation are similar to those in an acid-base titration.

1. Calculate the number of moles of sodium thiosulfate used in the titration, from the known volume and concentration.
2. Calculate the number of moles of iodine that reacted with this.
   I_2 (aq) + $2S_2O_3^{2-}$ (aq) → $2I^-$ (aq) + $S_4O_6^{2-}$ (aq)

   The equation for the reaction shows that 1 mole of iodine reacts with 2 moles of thiosulfate, so you need to divide the number of moles of thiosulfate by 2.

3. The equation for the reaction between iodate (V) and iodide ions is
   IO_3^- (aq) + $5I^-$ (aq) → $3I_2$ (aq) + $3H_2O$ (l)
   So, to find the number of moles of iodate(V) in 10 cm^3, you need to divide the number of moles of iodine by 3.
4. To find the number of moles of potassium iodate in the solid sample, it is the amount in the 100 cm^3 volumetric flask – so multiply by 10 because 10 cm^3 of the 100 cm^3 solution was taken in the pipette.
5. To find the mass, multiply by the molar mass of potassium iodate(V).

6. To calculate the percentage purity, divide by the mass of sample and multiply by 100.

d describe and carry out the following reactions:

i potassium halides with concentrated sulfuric acid, halogens and silver nitrate solution

ii silver halides with sunlight and their solubilities in aqueous ammonia solution

iii hydrogen halides with ammonia and with water (to produce acids)

i) Reaction of potassium halides with concentrated sulfuric acid

Reaction with potassium chloride with concentrated sulfuric acid

$KCl\ (s) + H_2SO_4\ (aq) \rightarrow KHSO_4 + HCl$

Potassium chloride reacts with concentrated sulphuric acid and forms steamy fumes of hydrogen chloride. This reaction can be used to prepare hydrogen chloride gas in the lab.

Reaction with potassium bromide with concentrated sulfuric acid

It produces hydrogen bromide but this gets further oxidized to prepare bromine and sulfur dioxide gas.

$KBr\ (s) + H_2SO_4 \rightarrow KHSO_4 + HBr$
then, $HBr + H_2SO_4 \rightarrow Br_2 + SO_2 + H_2O$

Reaction with potassium iodide with concentrated sulfuric acid

With potassium iodide, the hydrogen iodide formed is immediately oxidized to iodine. The sulfuric acid is reduced to sulfur dioxide, sulfur and hydrogen sulfide.

$KI + H_2SO_4 \rightarrow KHSO_4 + HI$
then, $2HI + H_2SO_4 \rightarrow I_2 + SO_2 + 2H_2O$
and, $6HI + H_2SO_4 \rightarrow 3I_2 + S + 4H_2O$
and, $8HI + H_2SO_4 \rightarrow 4I_2 + H_2S + 4H_2O$

Several observations can be made here:

i. Sulfur is seen as yellow solid.
ii. Hydrogen sulfide has a strong smell of bad egg.
iii. Iodine is produced as violet or purple vapour.

Test for halides: the silver halides

Different halide solutions form different coloured precipitates with silver nitrate solution. Adding aqueous ammonia solution can confirm the identification, because different halide precipitates have different solubilities in aqueous ammonia.

Potassium chloride with silver nitrate

$AgNO_3 + KCl \rightarrow KNO_3 + AgCl$

Chloride ions give a white precipitate of silver chloride, which darkens in sunlight. Also the precipitate dissolves to form a more stable compound in dilute ammonia solution.

Potassium bromide with silver nitrate

$AgNO_3 + KBr \rightarrow KNO_3 + AgBr$

Bromide ions give a cream precipitate of silver bromide, which darkens in sunlight. Also the precipitate dissolves to form a more stable compound in concentrated ammonia solution.

Potassium iodide with silver nitrate

$AgNO_3 + KI \rightarrow KNO_3 + AgI$

Iodide ions give a yellow precipitate of silver iodide, which does not darken in sunlight and does not dissolve in concentrated ammonia solution.

ii) *Follow "Test for halides" in (i)*

iii) Reactions of the hydrogen halides

To make pure samples of the hydrogen bromide and hydrogen iodide from their potassium salts, phosphoric (V) acid is used – it is not such a strong oxidizing agent as sulfuric acid.

With water

- All three hydrogen halides fume in moist air.
- All three are extremely soluble in water, forming acidic solutions

With ammonia

- All three react with ammonia to form a white smoke of the corresponding ammonia halide. e.g.:
  $NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$
  This is used as a test for the presence of hydrogen chloride gas.

e make predictions about fluorine and astatine and their compounds based on the trends in the physical and chemical properties of halogens.

- Going down the group the halogens get less reactive, so fluorine reacts with just about everything, and astatine is less reactive than iodine.
- Electronegativity decreases down the group, so astatine will have a low electronegative value.
- Fluorine will be most oxidizing.
- The compounds of fluorine and astatine with hydrogen should be soluble in water, forming acids.
- Bond enthalpies for carbon-hydrogen bonds decrease down the group. Fluorocarbon compounds should be the most stable, and astatocarbon compounds the least stable.

Topic 9: Introduction to Kinetics and Equilibria

a recall the factors that influence the rate of chemical reaction, including concentration, temperature, pressure, surface area and catalysts

Factors that influence the rate of chemical reaction are:

i. Concentration
ii. Temperature
iii. Pressure
iv. Surface area
v. Catalyst

b explain the changes in rate based on a qualitative understanding of collision theory

Collision theory: In order to occur a reaction, the following three conditions are needed:

i. Reacting particles must collide with each other.
ii. The reaction particles must have sufficient energy to break their existing bonds so that new bonds can be formed.
iii. The collision must be in the correct orientation.

Effect of concentration: When the concentration is increased, then more particles are available in per unit volume. So the frequency of successful collisions increases which results higher reaction rate.

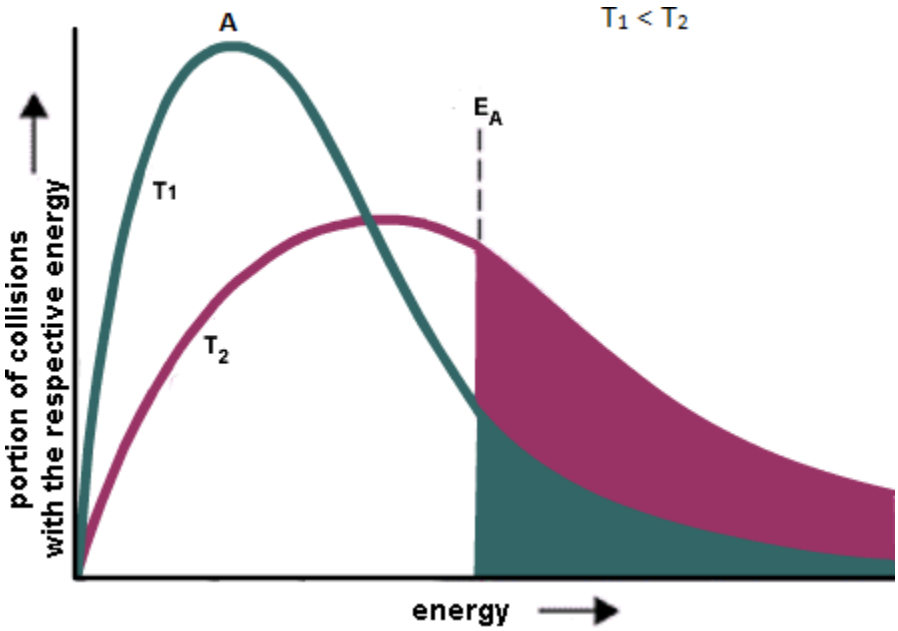
Effect of pressure: Increasing the pressure in a gas, the particles get close with each other in per unit volume. So, more successful collisions will take place which results higher reaction rate.

Effect of temperature: When the temperature is increased the particles gain kinetic energy to move faster, so the frequency of collisions also increase which results higher rate of reaction.

Effect of surface area: When the surface area is increased, more particles are exposed to be collided. So more successful collisions take place when the surface area is increased which results increased rate of reaction.

Effect of catalyst: Catalyst provides an alternative route with lower activation energy which enables mores successful collisions in per unit time, which results higher rate of reaction again.

c use, in a qualitative way, the Maxwell-Boltzmann model of the distribution of molecular energies to relate changes of concentration and temperature to the alteration in the rate of a reaction



The effect of temperature on a reaction mixture is to increase the energy of the particles. At a given temperature, the particles do not have on particular energy – but a range of energies. When the temperature increases, the distribution of molecular energies changes. These distribution is known as the Maxwell-Boltzman distribution.

Note that the x-axis measures energy; the y-axis measures the fraction of particles with a particular energy. Notice that:

- Energy marked A is the most common energy of the molecules.
- no molecules has zero energy
- each curve rises to a peak and then falls away to approach the x-axis without ever meeting it
- at higher temperature the peak of the graph is lower and moves to the right
- the area under the curve is the same at both temperatures because there are the same number of particles.

d demonstrate an understanding of the concept of activation energy and its qualitative relationship to the effect of temperature changes on the rate of reaction

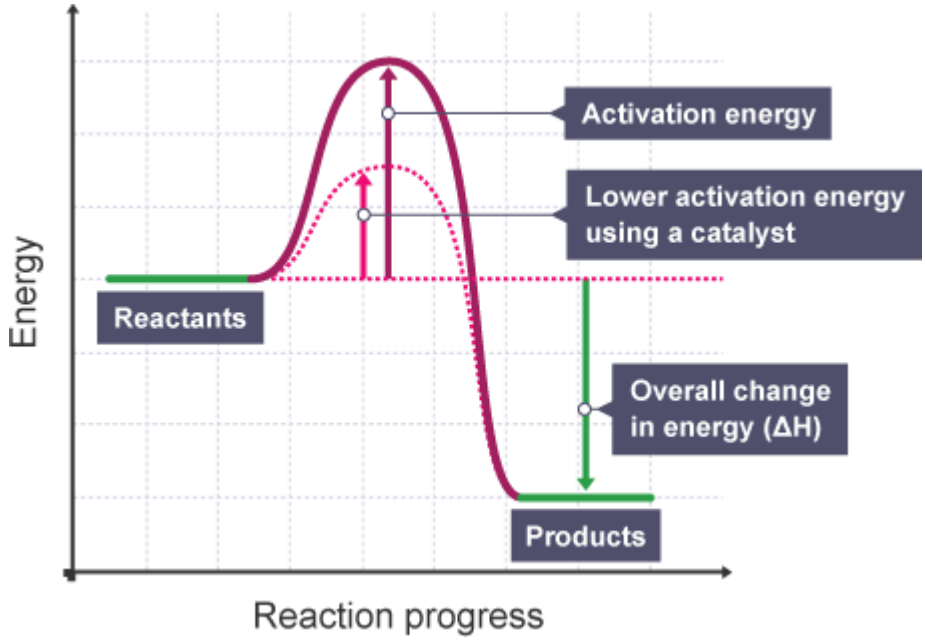
The energy barrier which is needed to overcome by reacting particles to start a reaction is called activation energy or the minimum energy which is required to start a chemical reaction is called activation energy.

For the Maxwell-Boltzman curve, we can see that at higher temperature, there are more molecules with higher energy – and in particular there are many more molecules with energy higher than the activation energy. This is the main reason why increasing the temperature of a reaction increases the reaction rate.

e demonstrate an understanding of the role of catalysts in providing alternative reaction routes of lower activation energy and draw the reaction profile of a catalysed reaction including the energy level of the intermediate formed with the catalyst

Catalyst provides an alternative route for a reaction, which have a lower activation energy.

Reaction profile diagram:



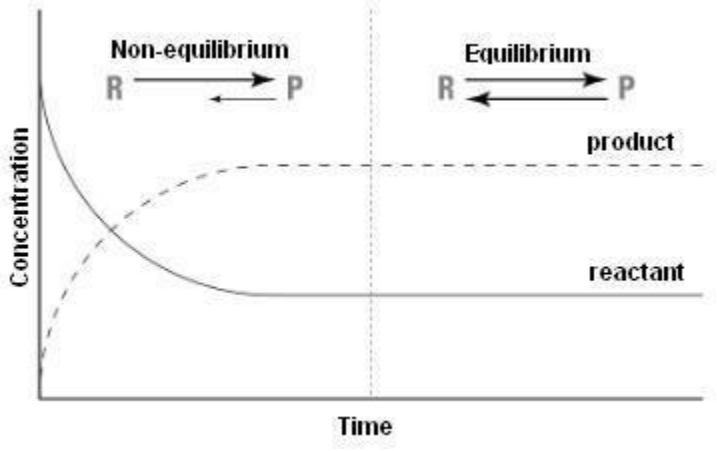
f carry out simple experiments to demonstrate the factors that influence the rate of chemical reactions, e.g. the decomposition of hydrogen peroxide.

Chemical Equilibria

a demonstrate an understanding that chemical equilibria are dynamic

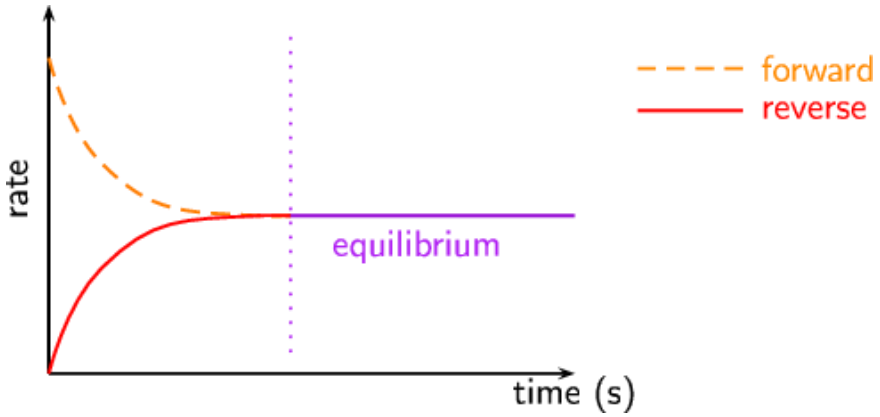
They can only be established in a closed system. In a equilibrium:

i. Reactions that do not go to completion. That means the concentration of reactants and products remain constant.



ii. The reactions are reversible.

iii. The reactions are dynamic. That means, in this position the forward reaction rate and the backward reaction rate is equal.



b deduce the qualitative effects of changes of temperature, pressure and concentration on the position of equilibrium, e.g. extraction of methane from methane hydrate

The effect of changes in conditions on equilibria is determined by applying **Le Chatelier's principle**. This states that:

"When a change is imposed on a chemical equilibrium, the reaction responds in such a way as to oppose the change. As a result, the **position of equilibrium** changes."

Position of equilibrium refers the concentration of reactants and products at the equilibrium state.

Factors:

Temperature: For an exothermic reaction increasing temperature shift the position of equilibrium to the left to reduce the extra heat effect by favouring the backward reaction which is endothermic.

Pressure: If the number of moles of reactants are greater than the product, then increasing pressure will shift the position of equilibria to right. Because when the pressure is increased the molecules which are higher in number will collide with each other, so to reduce the effect of pressure, the position shifts to the fewer molecules.

Concentration: Increasing the concentration of a reactant will make the reaction go forward as it can reduce the concentration of extra reactant added.

Catalyst: It has no effect on the position of equilibrium.

c interpret the results of simple experiments to demonstrate the effect of a change of temperature, pressure and concentration on a system at equilibrium, e.g.

i iodine(I) chloride reacting with chlorine to form iodine(III) chloride, or

ii $N_2O_4 \leftrightharpoons 2NO_2$.

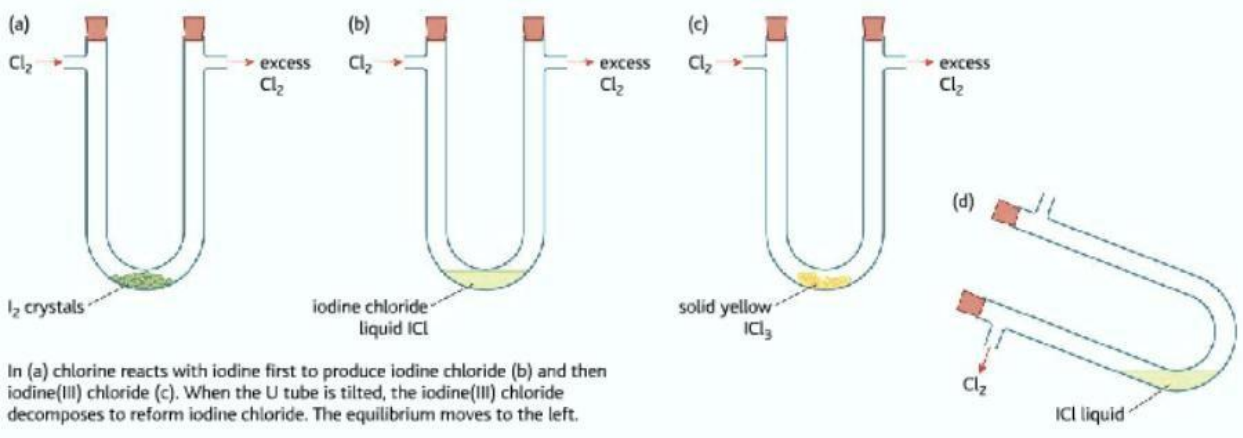
i) If chlorine gas is passed through a U-tube containing solid iodine, a brown liquid, iodine (I) chloride, ICl is formed with a brown vapour above it. The bottom of U-tube gets hot – the reaction is exothermic. If more chlorine gas is passed through a U-tube a yellow solid, iodine (III) chloride, ICl_3 is formed.

I_2 (s) + Cl_2 (g) → 2ICl(I)

ICl (I) + Cl_2 (g) ⇋ ICl_3 (s)

If the chlorine supply is removed, and the U-tube is tipped horizontal, the yellow crystals disappear and a brown gas is seen. The equilibrium is moving back to the left to reform and iodine (I) chloride and chlorine. These were separated from the reaction mixture when the U-tube was tipped. If the chlorine supply is attached again the yellow solid forms as the

equilibrium moves to the right, opposing the increase in chlorine concentration and producing iodine (III) chloride again.



In (a) chlorine reacts with iodine first to produce iodine chloride (b) and then iodine(III) chloride (c). When the U tube is tilted, the iodine(III) chloride decomposes to reform iodine chloride. The equilibrium moves to the left.

ii) Red-brown gas NO_2 exists in equilibrium with pale yellow N_2O_4.

$N_2O_4\ (g) \leftrightharpoons 2NO_2\ (g) \quad \Delta H = +58.1\ kJ\ mol^{-1}$

<u>Change in temperature</u>

The forward reaction between N_2O_4 and NO_2 is endothermic in the forward direction:

- When a closed tube containing the equilibrium mixture is put into hot water, the equilibrium is shifted to favour the production of NO_2 – the colour darkens.
- When the temperature is decreased, the equilibrium is shifted to favour the production of N_2O_4 – the colour pales.

<u>Change in pressure</u>

- an increase in pressure favours the production of N_2O_4 because that is the side with the smaller number of molecules – the colour pales.
- a decrease in pressure favours the production of NO_2, and an increase in the number of molecules – the colour darkens.

Topic 10: Organic Chemistry: Halogenoalkanes, Alcohols and Spectra

1 Alcohols

a give examples of, and recognise, molecules that contain the alcohol functional group

Alcohol is an alkane in which one hydrogen is replaced by an OH functional group. The general formula for alcohol is $C_nH_{2n+1}OH$.

b demonstrate an understanding of the nomenclature and corresponding structural, displayed and skeletal formulae of alcohols, and classify them as primary, secondary or tertiary

Nomenclature

Naming rules are the same as alkanes except:

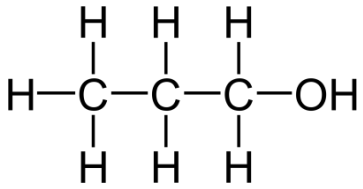
- the names end in –ol instead of –ane, so ethane becomes ethanol.
- you need to give the position of the OH group (the number of carbon atom it is attached to) before –ol in the usual way.

Classification

There are two types of alcohol:

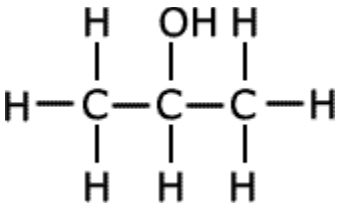
1. **Primary alcohol:** Two hydrogens atoms are attached to the carbon atom containing the OH group is called primary alcohol.

e.g. Propan – 1 – ol



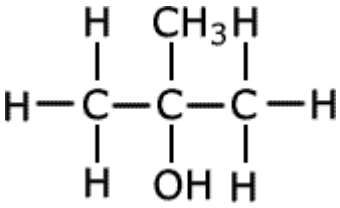
2. **Secondary alcohol**: One hydrogen atom is attached to the carbon atom containing OH group is called secondary alcohol.

e.g. Propan – 2 - ol



3. **Tertiary alcohol**: No hydrogen atoms is attached to the carbon atom containing OH group.

e.g. 2 – methyl propan-2-ol



c describe the following chemistry of alcohols:

i combustion

ii reaction with sodium

iii substitution reactions to form halogenoalkanes, including reaction with and its use as a qualitative test for the presence of the –OH group

iv oxidation using potassium dichromate(VI) in dilute sulfuric acid on PCl_5 primary alcohols to produce aldehydes and carboxylic acids and on secondary alcohols to produce ketones

i) The simplest oxidation reaction of alcohols is combustion to release energy. Complete combustion results in the formation of carbon dioxide and water vapour only. For example:

$C_2H_5OH\ (l) + 3O_2\ (g) \rightarrow 2CO_2\ (g) + 3H_2O(g)$

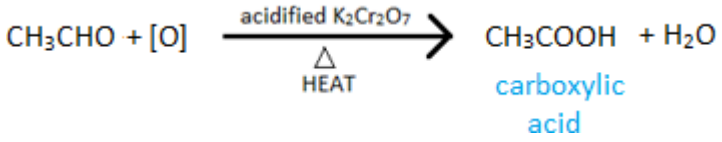
ii) Alcohols react with solid sodium. The sodium disappears, bubbles of gas form, and a white solid product forms. For example, with propan-1-ol:

$CH_3CH_2CH_2OH\ (l) + Na\ (s) \rightarrow CH_3CH_2CH_2O^-Na^+ + ½\ H_2\ (g)$

iv) The **primary alcohols** oxidizes to aldehyde when heated with acidified potassium dichromate (VI).

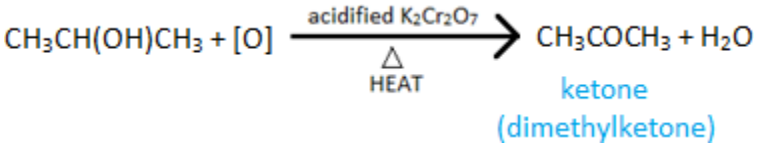
$$C_2H_5OH + [O] \xrightarrow[\text{HEAT}]{\text{acidified } K_2Cr_2O_7,\ \triangle} CH_3CHO \text{ [aldehyde, ethanal]} + H_2O$$

In further oxidation, the aldehydes converts to carboxylic acid.



During this reaction the colour of the solution turns from orange to green.

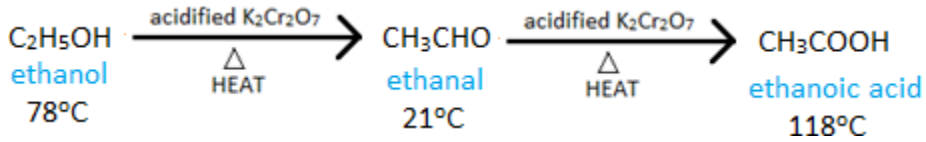
The **secondary alcohol** oxidizes to ketone when reacted with acidified potassium dichromate (VI).

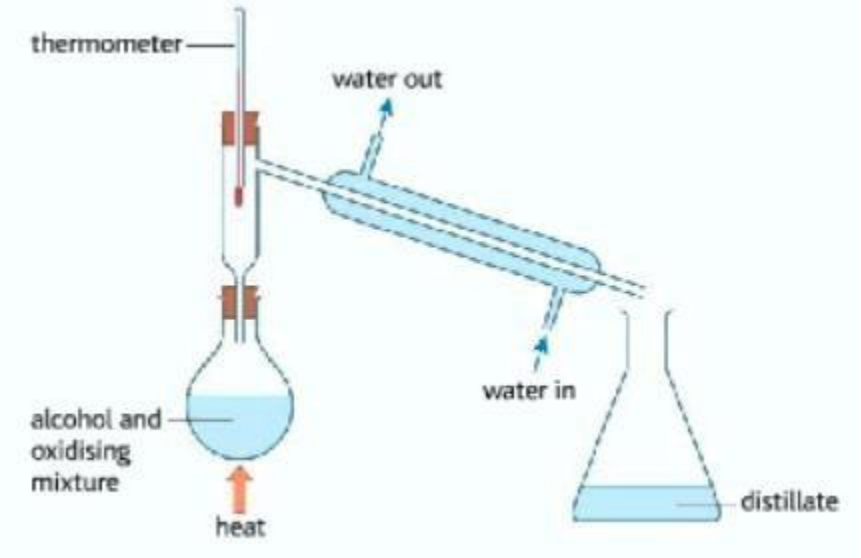


The colour turns from orange to green.

Tertiary alcohol cannot be oxidized.

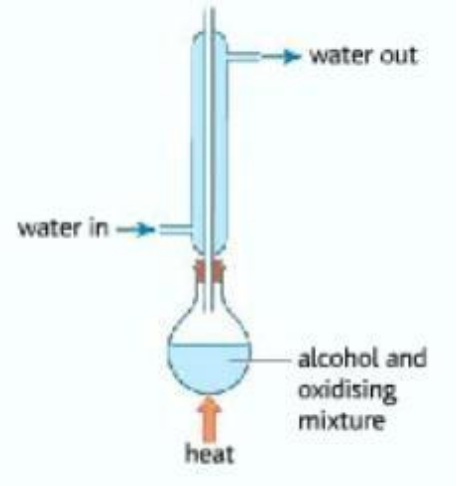
d demonstrate an understanding of, and practise, the preparation of an organic liquid (reflux and distillation), e.g. oxidation of alcohols.





Using simple distillation in the apparatus above, ethanol is oxidized to ethanol, and providing the temperature on the thermometer is above 21^{o}C and below 70^{o}C the distillate is ethanol. It is removed from the mixture before it has the change to be oxidized further.

In order to convert ethanol into ethanoic acid, the apparatus in the figure below can be used. The flusk contains ethanol and excess acidified potassium dichromate (VI). The vertical reflux condenser prevents ethanol, ethanol and ethanoic acid vapours from leaving the flusk. After the flask has been heated for some time, all of the ethanol will be converted into ethanoic acid. the apparatus above can then be used to distill off the ethanoic acid.



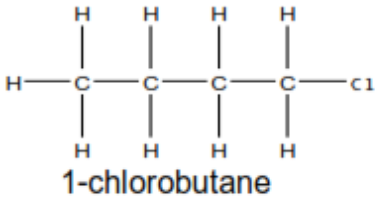
2 Halogeno Alkanes

a demonstrate an understanding of the nomenclature and corresponding structural, displayed and skeletal formulae for halogenoalkanes, including the distinction between primary, secondary and tertiary structures

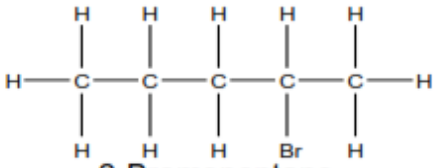
Halogenoalkanes contain a halogen as the functional group R-Hal.

The first part of the name of an halogenoalkane gives the position and name of the halogen concerned.

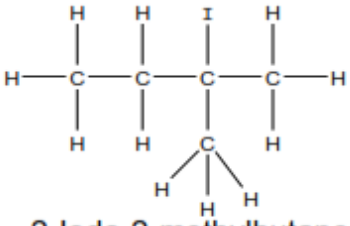
The second part of the name is based on the rest on the hydrocarbon structure.



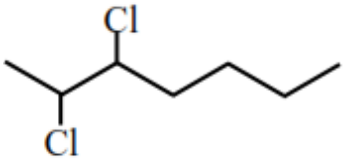
1-chlorobutane



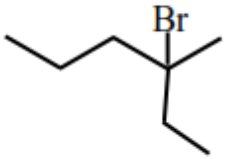
2-Bromopentane



2-Iodo-2-methylbutane

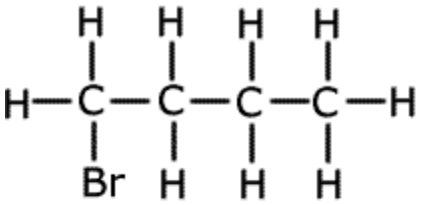


2,3-Dichloroheptane

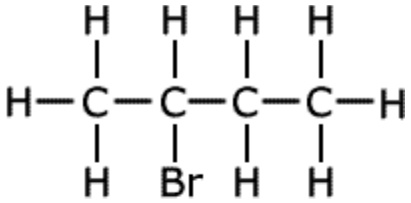


3-Bromo-3-methylhexane

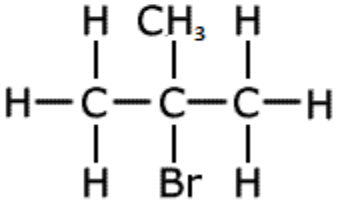
b interpret given data and observations comparing the reactions and reactivity of primary, secondary and tertiary compounds



1-bromobutane



2-bromobutane



2-bromo-2-methylbutane

1-bromobutane is a primary halogenoalkane.
2-bromobutane is a secondary halogenoalkane and
2-bromo-2-methylpropane is a tertiary halogenoalkane.

Three test tubes are set up as containing the three bromobutanes plus 1 cm^3 of ethanol which is the solvent. This time it is not necessary to warm the solutions. Just add 1 cm^3 of silver nitrate solution and shake the tubes. Leave them to stand and time how long it takes for them to go cloudy.

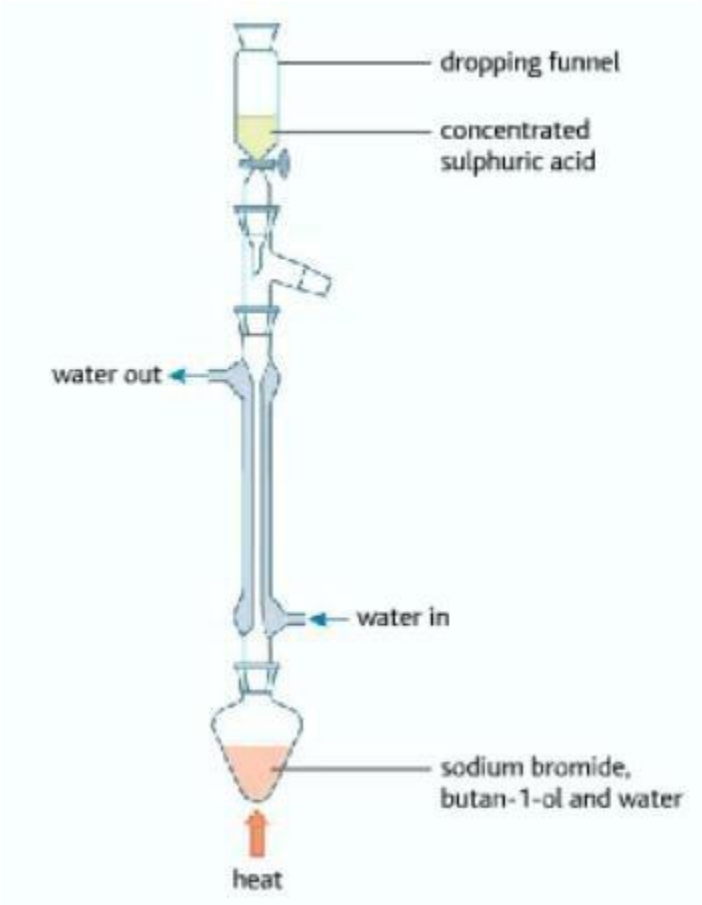
The result of this show that the reaction with tertiary halogenoalkane is faster than with secondary halogenoalkane which is in turn faster than with primary halogenoalkane.

c carry out the preparation of an halogenoalkane from an alcohol and explain why a metal halide and concentrated sulfuric acid should not be used when making a bromoalkane or an iodoalkane

Halogenoalkanes can be prepared by reacting metal halide and concentrated sulfuric acid mixture with alcohol. In this reaction, two steps of reaction take place:

i. $NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$
ii. $HCl + CH_3CH_2OH \rightarrow CH_3CH_2Cl + H_2O$

The alcohol is heated under the reflux with the reactants to make halegenoalkane. The halegenoalkane made is distilled from the reaction mixture and collected as oily droplets under water.



By using this method bromoalkane and iodoalkane cannot be prepared. Because concentrated sulfuric acid is relatively strong oxidizing agent. It is not strong enough to oxidize HCl but it will oxidize and decompose HBr and HI. So any HBr or HI formed in the reaction between sodium bromide and sodium iodide and concentrated sulfuric acid undergoes further reaction.

For bromine,

i. $NaBr + H_2SO_4 \rightarrow NaHSO_4 + HBr$
ii. $2HBr + H_2SO_4 \rightarrow Br_2 + SO_2 + 2H_2O$

For iodine,

i. $NaI + H_2SO_4 \rightarrow NaHSO_4 + HI$
ii. $2HI + H_2SO_4 \rightarrow I_2 + SO_2 + H_2O$

or,

$6HI + H_2SO_4 \rightarrow 3I_2 + S(s) + H_2O$

or,

$HI + H_2SO_4 \rightarrow I_2 + H_2S + H_2O$

Sulfur is seen as yellow solid. Hydrogen sulfide has a strong smell of bad egg. Iodine is produced as a purple vapour.

<u>Iodoalkane preparation</u>

For bromoalkane and iodoalkane we can make the phosphorus (III) halide or (PI_3/PBr_3) by using red phosphorus with bromine or iodine. This are warmed under reflux with the alcohol.

$3C_2H_5OH + PI_3 \rightarrow 3C_2H_5I + H_3PO_3$

d describe the typical behaviour of halogenoalkanes. This will be limited to treatment with:

i aqueous alkali, e.g. KOH (aq)

ii alcoholic potassium hydroxide

iii water containing dissolved silver nitrate

iv alcoholic ammonia

i) Reaction with aqueous alkali, such as potassium hydroxide, to form an alcohol.

$CH_3CH_2CH_2CH_2Br$ (l) + KOH (aq) $\rightarrow$ $CH_3CH_2CH_2CH_2OH$ (aq) + KBr (aq)
1-bromobutane butan-1-ol

ii) Reflux/heat with concentrated alcoholic alkali to form an alkene.

$CH_3CH_2CH_2CH_2Br + KOH$ (alc) $\rightarrow$ $CH_3CH_2CH{=}CH_2 + KBr + H_2O$
1-bromobutane but-1-ene

iii) Add 1 cm^3 ethanol in a test tube along with 1 cm^3 of silver nitrate and 5 drops of halogenoalkane.

Results:

1-chlorobutane → white precipitate
1-bromobutane → pale yellow precipitate
1-iodobutane → yellow precipitate

The result of the investigation will confirm that the rate of hydrolysis of halogenoalkanes increases in order:

1-chlorobutane **<** 1-bromobutane **<** 1-iodobutane

iv) Halogenoalkane with alcoholic ammonia gives nucleophilic substitution reaction.

$CH_3CH_2I + NH_3$ (alc) → $CH_3CH_2NH_2 + HI$
ethylamine

$CH_3CH_2NH_2 + CH_3CH_2I \rightarrow (CH_3CH_2)_2NH + HI$
diethylamine

$(CH_3CH_2)_2NH + CH_3CH_2I \rightarrow (CH_3CH_2)_3N + HI$
triethylamine

$(CH_3CH_2)_3N + CH_3CH_2I \rightarrow (CH_3CH_2)N^+I^-$
tetraethylammonium iodide

e carry out the reactions described in 2.10.2d i, ii, iii

f discuss the uses of halogenoalkanes, e.g. as fire retardants and modern refrigerants.

Because halogenoalkanes, likes alkanes, are generally unreactive and, unlike alkanes, do not burn easily. They are used as fire retardants and as refrigerants.

The chloroflurocarbons (CFCs) used commonly in the past were found to seriously deplete the ozone layer in the atmosphere. This depletion enables more harmful UV radiation to reach the surface of the Earth, which increases the risk of skin cancer and eye cataracts.

Because they are unreactive, the CFCs are eventually carried through to the ozone layer, which they affect by a series of free-radical reactions. This is why CFCs are being phased out – other halogenoalkanes, such as hydroflurocarbons (HFCs) that do not release free radicals, are being used as safer alternatives.

Mechanism

a classify reactions (including those in Unit 1) as addition, elimination, substitution, oxidation, reduction, hydrolysis or polymerization

Addition: When two or more substances combine to form one product, then this type of reaction is called addition reaction.

$$C_2H_4 + Br_2 \rightarrow C_2H_4Br_2$$

Elimination: When one reactant reacts to produce a new substance and a small molecule such as water or hydrogen bromide then this type of reaction is called elimination reaction.

$$CH_3CH_2\text{-}CH_2Br + KOH\ (aq) \rightarrow CH_3CH{=}CH + KBr + H_2O$$

Substitution: When a group of atoms is replaced by another atom then this reaction is called substitution reaction.

$CH_3CH_2CH_2Cl + KOH(aq) \rightarrow CH_3CH_2CH_2OH + KCl$

Oxidation: Addition of oxygen during a chemical reaction is called oxidation.

$$CH_3CH_2OH + [O] \rightarrow CH_3COOH + H_2O$$

Reduction: The removal of oxygen or the addition of hydrogen atoms to a molecule is reduction.

$$CH_3COCH_3 + [H] \xrightarrow[\text{or } NaBH_4]{LiAlH_4} CH_3 - \underset{\displaystyle OH}{\underset{|}{CH}} - CH_3$$

Hydrolysis: When a molecule is broken down by the addition of water.

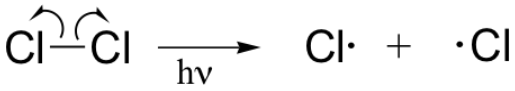
$$CH_3\underset{\displaystyle Cl}{\underset{|}{CH}}CH_3 + KOH \longrightarrow CH_3 - \underset{\displaystyle OH}{\underset{|}{CH}} - CH_3 + Cl^-\ (aq)$$

Polymerization: When many small identical molecules join to form a large molecule then this reaction is called polymerization.

$$n\ CH_2{=}CH_2 \longrightarrow \left(CH_2 - CH_2 \right)_n$$

b demonstrate an understanding of the concept of a reaction mechanism and that bond breaking can be homolytic or heterolytic and that the resulting species are either free radicals, electrophiles or nucleophiles

Homolytic fission: When a bond breaks and one of the atom keeps one of the shared electron pair, it is called homolytic fission.



Heterolytic fission: When a bond breaks and both of the electrons are kept by one of the atom, it is called Heterolytic fission. This forms a positive ion and a negative ion.

c give definitions of the terms free radical, electrophile and nucleophile

Free radical: A free radical is an atom or molecule that has a single unpaired electron in its outer shell. Free radical forms when homolytic fission takes place.

Electrophile: Electrophiles are either electron deficient centered or positively charged. It receives a pair of electron to form a covalent bond.

Nucleophile: Nucleophiles are positively charged or electron-rich centered. It donates a pair of electrons to form a new covalent bond.

d demonstrate an understanding of why it is helpful to classify reagents

A reaction takes place in various steps. The rate of reaction and the type of products depend on the nature of reagents. That's why to understand the mechanism of a chemical reaction, classification of reagents are needed.

e demonstrate an understanding of the link between bond polarity and the type of reaction mechanism a compound will undergo

For polar bonds, heterolytic fission will take place.

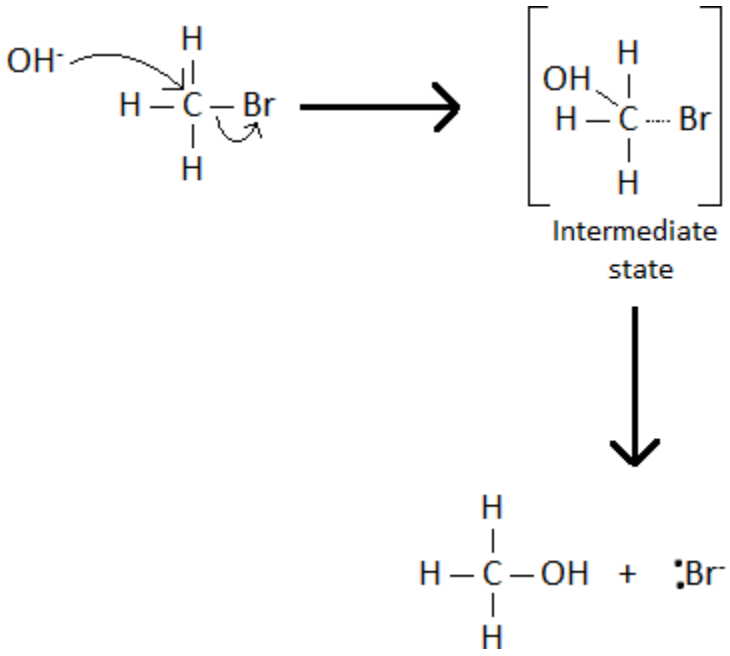
For non-polar bonds such as carbon-hydrogen bond will usually undergo homolytic fission but not always.

A nucleophile can attack the positive atom in the polar bond. An electrophile can attack an electron-rich part of a molecule. e.g. carbon-carbon double bond in alkenes.

f describe the mechanisms of the substitution reactions of halogenoalkanes and recall those in 1.7.2e and 1.7.3e

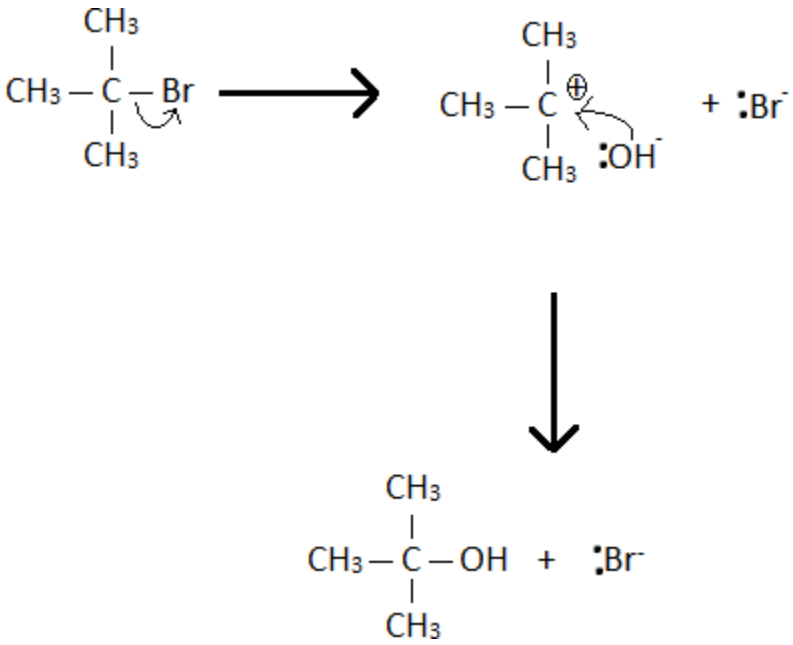
For **primary halogenoalkanes** S_N2 mechanism takes place.

In S_N2, S represents substitution,
N represents nucleophile,
2 represents the no. of species (the halogenoalkane molecule and hydroxide ion) involved in the reaction.



The C — Br bond in the halogenoalkane is polar. C is partially positive and Br is partially negative. OH^- acts as a nucleophile, gets attracted to C and attacks. The OH^- donates an electron pair to the carbon and stars to form a bond. The C — Br bond gets broken.

For **tertiary halogenoalkanes**, S_N1 mechanism takes place.



A small proportion of halogenoalkane ionizes to give a carbocation and a bromide ion. The lone pair of the nucleophile (hydroxide ion in this case) is attracted to the positive carbon and moves towards it to create a new bond.

g demonstrate an understanding of how oxygen, O_2, and ozone, O_3, absorb UV radiation and explain the part played by emission of oxides of nitrogen, from aircraft, in the depletion of the ozone layer, including the free radical mechanism for the reaction and the fact that oxides act as catalysts.

Ozone layer protects the Earth from harmful UV radiation. Ozone is formed when oxygen molecules absorb the energy from UV light, and splits into two oxygen free radicals.

$O = O \rightarrow 2\ O\bullet$

These free radicals then recombine with oxygen to form ozone.

$O_2 + O\bullet \rightarrow O_3$

But these ozone is being broken down because of reacting with CFCs, NO and NO_2 released from cars and jet engines. Although CFCs are very stable molecules, but in the higher atmosphere the UV radiation causes the C-Cl bond to break and form Cl• radicals.

$CCl_2F_2 \rightarrow \bullet CClF_2 + Cl\bullet$

This chlorine free radical reacts with ozone.

$Cl\bullet + O_3 \rightarrow \bullet ClO + O_2$

The chlorate free radical then reacts with ozone to form more chlorine free radicals.

$\bullet ClO + O_3 \rightarrow 2O_2 + Cl\bullet$

Since the Cl• regenerates and remains unchanged, it is a catalytical radical. So a single Cl• radical can breakdown a huge amount of ozone molecules.

In the same way, oxides of nitrogen also damage the ozone layer by producing NO• radicals.

$NO\bullet + O_3 \rightarrow NO_2 + O_2$

This radical then regenerates.

$NO_2 + O\bullet \rightarrow NO\bullet + O_2$

NO• is also a catalytical radical in this case.

a interpret fragment ion peaks in the mass spectra of simple organic compounds, e.g. the difference between propanal and propanone

Mass spectrum of butane

Butane, $CH_3CH_2CH_3$ breaks into the following fragment ions:

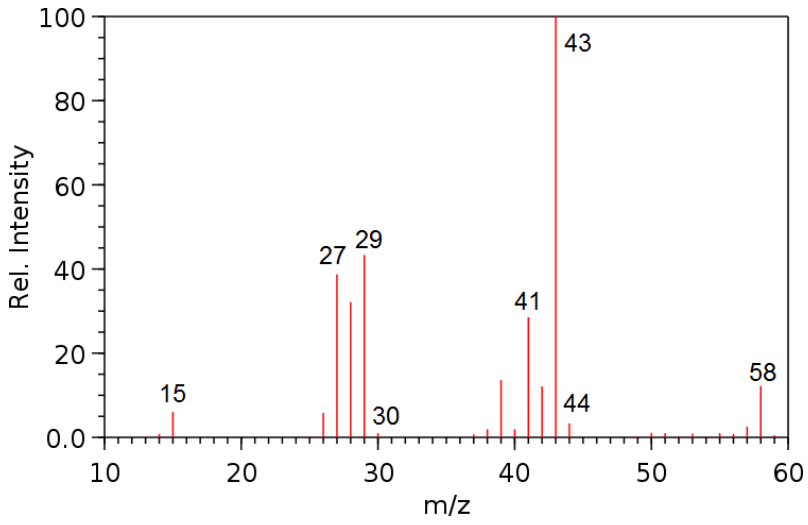
$^+CH_3$ m/z = 15

$^+CH_2CH_3$ m/z = 29

$CH_3CH_2CH_2^+$ m/z = 43

$CH_3CH_2CH_3^+$ m/z = 58

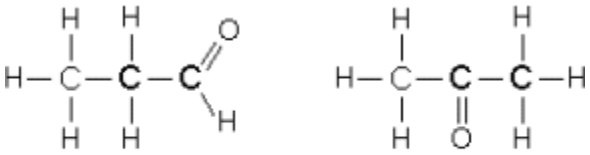
It is represented in the mass spectrum of butane:



Here the peak with the highest m/z value corresponds to the ion with the largest mass.

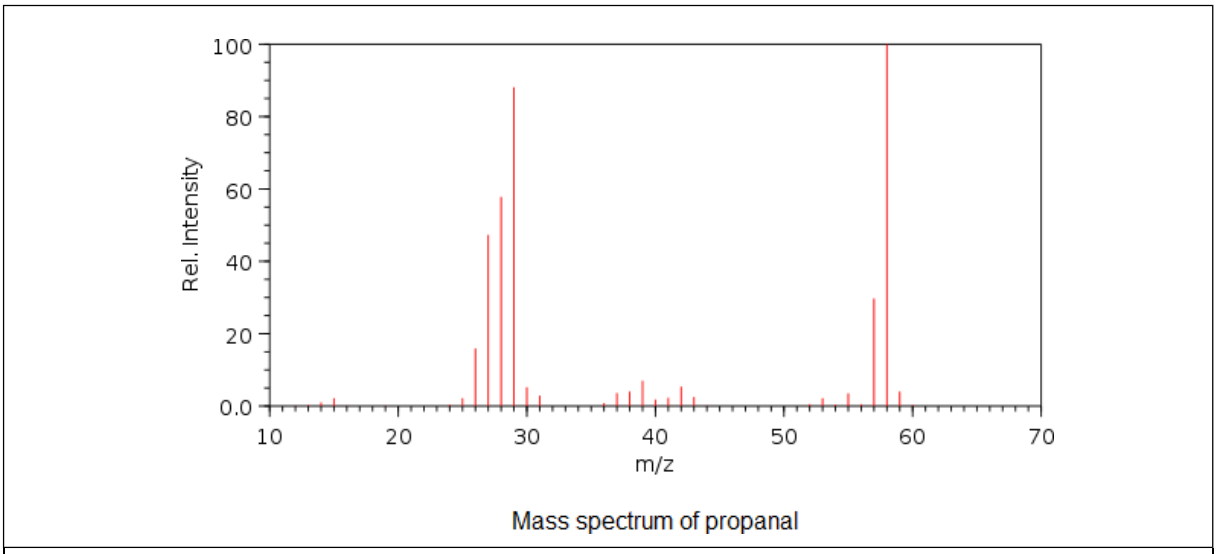
The peak with the highest intensity is base ion peak.

Mass spectra of propanal and propanone

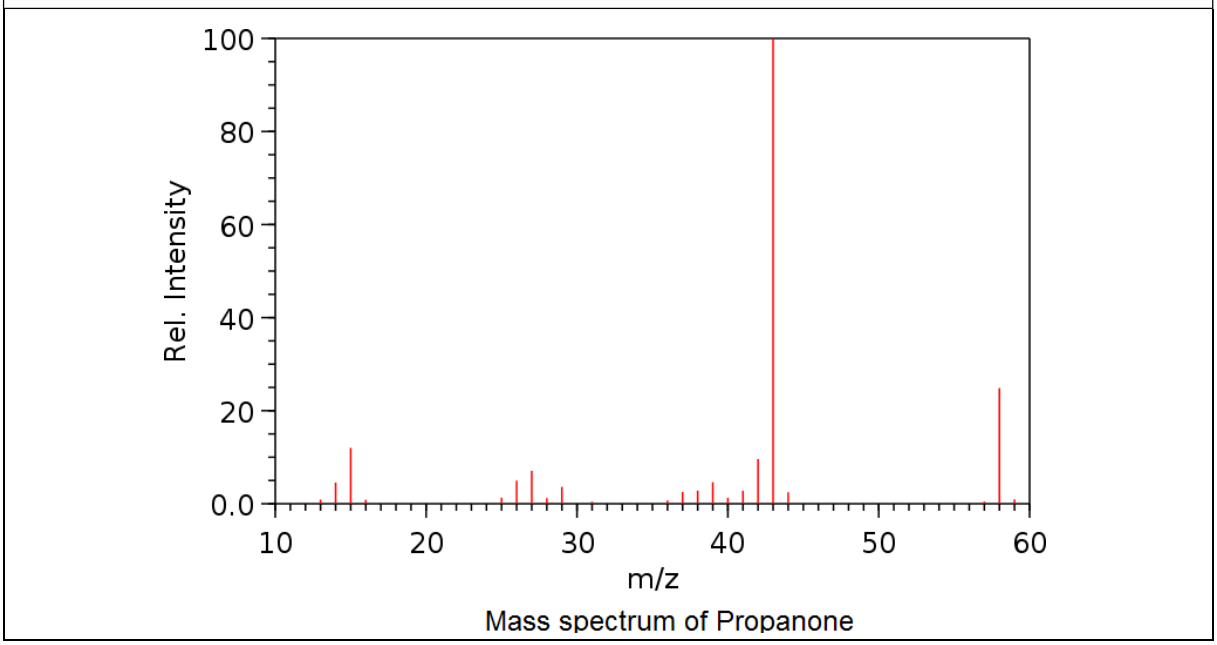


propanal propanone

Propanal is an aldehyde and propanone is a ketone. But both of them has the same relative molecular mass. To find their characteristic difference, we need to take a look at their mass spectra.



Mass spectrum of propanal



Mass spectrum of Propanone

Difference:

For propanal, at 29 m/z a peak for $CH_3CH_2^+$ will be given which will not be present in propanone.

For propanone, there will be a peak at 43 for CH_3CO^+ which will not be present in propanale.

In both spectrum, there will be peaks at 58 m/z. But for propanale there will be a peak at 57.

b use infrared spectra, or data from infrared spectra, to deduce functional groups present in organic compounds and predict infrared absorptions, given wavenumber data, due to familiar functional groups. This will be limited to:

i C–H stretching absorptions in alkanes, alkenes and aldehydes
ii O–H stretching absorptions in alcohols and carboxylic acids
iii N–H stretching absorption in amines
iv C=O stretching absorptions in aldehydes and ketones
v C–X stretching absorption in halogenoalkanes
vi as an analytical tool to show the change in functional groups during the oxidation of an alcohol to a carbonyl

c demonstrate an understanding that only molecules which change their polarity as they vibrate can absorb infrared radiation

Molecules that change their polarity as they vibrate (due to the movement of the dipoles in the polar bonds) absorb infrared radiation.

d demonstrate an understanding that H_2O, CO_2, CH_4 and NO molecules absorb IR radiation and are greenhouse gases, whilst O_2 and N_2 are not.

Oxygen and nitrogen do not change their polarity. So they do not absorb IR radiation unlike water, carbon dioxide, methane and nitrogen monoxide and therefore they are not greenhouse gases.

Green Chemistry

a demonstrate an understanding that the processes in the chemical industry are being reinvented to make them more sustainable ('greener') by:

i changing to renewable resources

ii finding alternatives to very hazardous chemicals

iii discovering catalysts for reactions with higher atom economies, e.g. the development of methods used to produce ethanoic acid based on catalysts of cobalt, rhodium and iridium

iv making more efficient use of energy, e.g. the use of microwave energy to heat reactions in the pharmaceutical industry

v reducing waste and preventing pollution of the environment

i) Changing to renewable sources

If renewable resources replace non-renewable materials raw materials will be conserved and the process becomes more sustainable. Plants can be used as a source of certain organic compounds instead of oil. These can be extracted directly from plants or derived from processing plant material, such as using fermentation to produce ethanol from plant starch and sugars.

ii) Finding alternatives to hazardous chemicals

This involves replacing dangerous chemicals used in a process with less harmful chemicals which can do the same job. It includes changing processes so that less risky reagents are used or less destructive intermediates are formed. It also includes using less damaging solvents for a process.

iii) Discovering catalysts for reactions with higher atom economies

Introduction of more efficient catalyst enables lower temperatures and pressure to be used and so saves energy. More efficient catalysts create fewer bye-products and so reduce waste.

iv) Making more efficient use of energy

Changing the processes that use lower pressures and temperatures reduce the energy required to make a given product. Use of exothermic reactions to provide heat reduces the amount of non-renewable energy used, for example introducing a heat transfer system (using hot

products to heat incoming reactants). Use of microwaves instead of hotplates allows more efficient heating, as it heats the relevant molecules directly.

v) Reducing waste and preventing pollutions of the environment

Recycling materials means that less waste is produced. Making biodegradable products means that they can be broken down by natural processes and so reduce the materials that need to be treated after use.

b discuss the relative effects of different greenhouse gases as absorbers of IR and hence on global warming

Infrared radiation emitted from the Sun is at first absorbed by the Earth's surface. This heats the Earth and release the radiation but with longer wavelength. Greenhouse gases absorb this longer wavelength IR and warms up the atmosphere. Carbon dioxide, water vapour and methane are the main greenhouse gases. This contributes to global warming.

The relative greenhouse factors of different gases compares the effect that different gases have in absorbing IR radiation compared with carbon dioxide.

Carbon dioxide ——————— 1
Methane ———————————30
Nitrogen oxides ——————— 160
Dinitrogen oxide ——————— 200
Trichlorofluromethane ——— 21000

The net effect of individual greenhouse gases and hence on global warming is determined by two properties:

i. Their ability to absorb IR radiation.
ii. Their half-life in the atmosphere.

c discuss the difference between anthropogenic and natural climate change over hundreds of thousands of years

Anthropogenic climate change occurs from the activities of human beings. e.g. burning fossil fuels, deforestation that increase levels of carbon dioxide, methane and dionitrogen oxide (N_2O), from aircraft exhausts over relatively short timescales.

Natural climate change is due to natural processes such as the dissolving of carbon dioxide in sea water or the formation of carbonates in rocks that remove carbon dioxide in sea water or the formation of carbonates in rocks that remove carbon dioxide from the atmosphere over

much longer timescales. Other natural process, such as volcanic eruptions or changes in solar activity, can also cause climate change.

d demonstrate understanding of the terms carbon neutrality and carbon footprint

A fuel is called **carbon-neutral** when the same amount of carbon dioxide it released while manufacturing and burning is absorbed from the atmosphere as the raw material is grown or the fuel formed. Only certain biofuels can be considered as carbon neutral within a human lifetime. Fossil fuels are formed on geological timescales. A carbon-neutral process occurs when there is not net carbon dioxide emission to the atmosphere. Emissions are balanced by actions that remove an equivalent amount of carbon dioxide.

The **carbon footprint** of a fuel is the total mass of carbon dioxide produced from a fuel as it is manufactured and then burnt, in units of g kJ^{-1}. For biofuels such as those made from sugar or vegetable oils, the amount of carbon dioxide that was absorbed in growing the raw material for the fuel should be subtracted from this total mass. A carbon footprint in general is a measure of the amount of carbon dioxide emitted through the use of fossil fuels. It is often measured in tonnes of carbon dioxide, and can be calculated for an individual, a household, an organization or over a product **lifecycle** for manufactured goods.

e apply the concept of carbon neutrality to different fuels, such as petrol, bioethanol and hydrogen

When a tree grows it absorbs carbon dioxide from the atmosphere. When the tree is burned it releases the same amount of carbon dioxide as it absorbed. So this process is carbon neutral.

Petroleum fuels were formed millions of years ago by microorganisms which captured carbon dioxide from the atmosphere. These fuels produce carbon dioxide when they burn. Since the carbon dioxide absorbed cannot be set against the carbon dioxide produced within a reasonable time span, say 50 years, so they are not considered to be carbon neutral.

Biofuels, such as bioethanol produced from maize, are also not carbon neutral. Although the maize absorbs carbon dioxide when it grows, the stages in the production of the bioethanol require energy. Unless this energy is generated without releasing carbon dioxide, producing biofuels gives out more carbon dioxide than the crop absorbs.

Burning hydrogen only produces water and no carbon dioxide. However, it is still not carbon neutral. Because hydrogen has to be manufactured chemically from natural gas or by electrolysis of water. Either way, there is some carbon dioxide produced in these steps.

f discuss and explain, including the mechanisms for the reactions, the science community's reasons for recommending that CFCs are no longer used due to their damaging effect on the ozone layer.

Follow g in the Mechanism chapter